

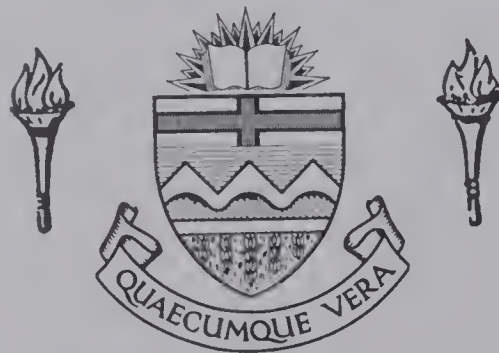
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THE ENERGY TRANSFER MECHANISM IN MERCURY PHOTSENSITIZATION

by

STEPHEN PENZES



A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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March, 1968

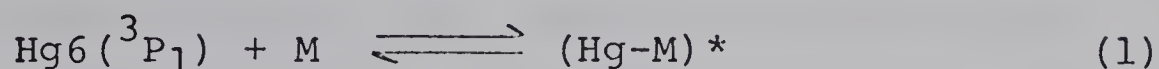
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FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled THE ENERGY TRANSFER MECHANISM IN MERCURY PHOTOSENSITIZATION submitted by Stephen Penzes in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

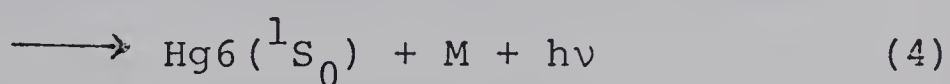
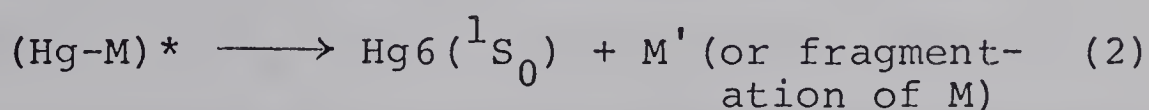
ABSTRACT

The detailed mechanism of energy transfer reactions in triplet mercury photosensitizations has been investigated.

The intervention of an electronically excited transient complex molecule in the energy transfer process has been demonstrated. It is proposed that the complex formation



is the primary step of energy transfer. The main decomposition routes of the intermediate complex are



The photon originates from reaction (4) at longer wavelengths than that of the primary light, 2537Å. The observation of this emission is an indication of an intermediate formation. The participation of reaction (3) was shown by detecting the mercury metastable atoms,

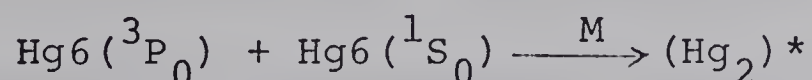


Absolute rate constant values were obtained for a number of molecules for $\text{Hg6}(^3\text{P}_1)$ and for $\text{Hg6}(^3\text{P}_0)$ atoms.

The experimental observations make it possible to deduce correlations between structural variations in the acceptor molecule and the efficiency of the various elementary processes.

In the light of this information it then becomes possible to give an outline of the main features of the 3P_1 atom quenching reactions in terms of a simplified potential energy diagram, incorporating light emission, transitions to the 3P_0 and 1S_0 levels and redissociation along the 3P_1 contour as simultaneous competing reactions. The model considered is capable of accounting in a qualitative manner for most of the experimental facts of mercury photosensitizations.

The decay of 3P_0 atoms in non-reactive media has been studied as well. The most important route of decay is via diatomic excimer formation in a third order reaction,



Careful studies of the excimer emission kinetics provided compelling evidence that the two emission bands of the excimer arise from two different electronic transitions.

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TABLE OF CONTENTS

	<u>PAGE</u>
ABSTRACT.....	i
ACKNOWLEDGEMENTS.....	iii
TABLE OF CONTENTS.....	iv
LIST OF TABLES.....	viii
LIST OF ILLUSTRATIONS.....	ix
CHAPTER I: INTRODUCTION AND LITERATURE SURVEY	
1) Fundamentals of photosensitization	1
2) a. Mercury as a photosensitizer	5
b. Quenching of the mercury resonance radiation.	7
c. The measurement of 3P_1 quenching cross section	9
i. physical method	
ii. chemical method	
d. The partial quenching of 3P_1 state	17
e. The detection of 3P_0 atoms	18
f. The removal of 3P_0 atoms	22
i. the emission of the forbidden line 2654A	
ii. deactivation on the wall; reactivation to the 3P_1 level via energetic collisions	
iii. quenching by the substrate	
iv. quenching by ground state mercury atoms.	
3. Correlation of energy transfer efficiencies with the molecular parameters of the acceptor.	29

CHAPTER II: EXPERIMENTAL

PAGE

- | | | |
|----|---|----|
| 1) | The measurement of 3P_1 quenching by the physical method | 39 |
| | i) Principle | |
| | ii) Description of the apparatus | |
| | iii) Calibration and general operating conditions. | |
| 2) | The measurement of 3P_0 concentration by the 4047 absorption technique and detection of the Hg_2^* emission. | 49 |
| | i) Principle | |
| | ii) Description of the apparatus | |
| | iii) Preliminary measurements | |
| | iv) Summary of operating conditions | |
| 3) | Measurement of emission from the intermediate complex (Hg-molecule)* | 61 |

CHAPTER III: RESULTS

- | | | |
|----|--|-----|
| 1) | Energy transfer involving an excited intermediate | 64 |
| 2) | The process $Hg^1 \xrightarrow{A} Hg$ | 80 |
| 3) | The process $Hg^1 \xrightarrow{A} Hg^0$ | 98 |
| 4) | A brief study of the process $Hg^1 + NH_3$
$Hg^1 + NH_3 \rightarrow Hg^0 + NH_3'$ | 111 |

	<u>PAGE</u>
5) The process $\text{Hg}^0 + \text{Hg} \xrightarrow{\text{N}_2} (\text{Hg}_2)^*$	113
i) Experimental arrangements and results	
ii) Discussion and Conclusions	
iii) The proposed reaction mechanism and the relation of nitrogen pressure to emission intensities.	
iv) Calculation of the rate constant for the process $\text{Hg}^0 + \text{Hg} \xrightarrow{\text{N}_2} (\text{Hg}_2)^*$	
6) The mercury excimer emissions from H_2O and D_2O systems	140
7) The process $\text{Hg}^0 \xrightarrow{\text{A}} \text{Hg}$	147
i) Results and Discussion	
ii) Calculation of the rate constant for the process $\text{Hg}^0 \xrightarrow{\text{A}} \text{Hg}$	
8) The comparison of Hg^1 quenching cross sections measured by the physical and by the chemical methods	163
Chapter IV: SUMMARY AND CONCLUSIONS	168
APPENDIX	
1) Calculation of the rate constants	174
2) The steady state treatment for the excimer emissions.	181
3) S. Penzes, A.J. Yarwood, O.P. Strausz and H.E. Gunning, "The Role of $\text{Hg}(^3\text{P}_0)$ Atoms in Mercury Photosensitization" J. Chem. Phys. <u>43</u> , 4524-6 (1966).	183

	<u>PAGE</u>
4) S. Penzes, O. P. Strausz and H. E. Gunning, "Fluorescence of Excited Complex Molecules in Mercury Photosensitization" J. Chem. Phys. <u>45</u> , (1966).	185
5) S. Penzes, O. P. Strausz and H. E. Gunning, "Kinetics of the "a" and "b" band Emissions of Mercury Excimers". J. Chem. Phys. (1968) in press.	187

BIBLIOGRAPHY.....;

VITA.....

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
1)	Relationship between pressure and quenching of calibration gases.	48
2)	Complementary list of compounds examined for complex intermediate emission.	67
3)	The quenching of resonance radiation and quenching cross section values.	90 - 92
4)	List of compounds tested for 4047A absorption during mercury photosensitization.	99
5)	Tabulation of data obtained for Hg-N ₂ system.	134
6)	Quenching cross section relationships of propanes obtained for Hg ¹ and Hg ⁰ atoms.	152
7)	Comparison of propane and neopentane quenching ratios obtained for Hg ¹ and Hg ⁰ atoms.	156
8)	Compounds that form metastable atoms and their quenching cross sections.	167

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>PAGE</u>
1)	The lower energy levels of mercury.	6
2)	The experimental arrangement and measuring cell for Hg^1 quenching cross section measurement.	40
3)	Experimental arrangement for the study of 4047A absorption and emission from Hg_2^* .	51
4)	The cell unit for the study of 4047A absorption and emission from Hg_2^* .	52
5)	Cell unit for the (Hg-molecule)* excited intermediate emission.	63
6)	Relative emission intensity vs.energy acceptor pressure.	65
7)	Relative emission intensity vs.substrate pressure (0-500 torr).	68
8)	A schematic representation of $\text{Hg}^1 + \text{RH}$ potential energy curves.	74
9 - 16)	Quenching plots for Hg^1 atoms.	81 - 88
17)	Relative concentrations of Hg^0 atoms in pure methanol.	101
18)	Relative concentrations of Hg^0 atoms in pure ethanol.	102
19)	Relative concentrations of Hg^0 atoms in pure propane.	103

<u>Figure</u>		<u>PAGE</u>
20)	Relative concentrations of Hg^0 atoms in pure n-butane.	104
21)	Relative concentrations of Hg^0 atoms in pure neopentane.	105
22)	Relative concentrations of Hg^0 atoms in pure cyclohexane.	106
23)	Relative concentrations of Hg^0 atoms in pure carbonmonoxide.	107
24)	NH_3 emissions.	114
25)	Mercury nitrogen system.	116
26)	$\text{I}(4850)/\text{I}(3350)$ in nitrogen system.	118
27)	3350A band intensity from nitrogen- ethane mixtures.	119
28)	3350A band intensity from nitrogen- propane mixtures.	120
29)	4850A band intensity from nitrogen- ethane mixtures.	121
30)	4850A band intensity from nitrogen- propane mixtures.	122
31)	Emission ratios at different concentrat- ions of ethane added to nitrogen.	123
32)	Emission rates at different concentrat- ions of propane added to nitrogen.	124

<u>Figure</u>		<u>PAGE</u>
33)	Intensity variation in N_2 -Xe mixtures (constant pressure 5 torr).	125
34)	Potential energy curves of Hg_2 molecule.	128
35)	Emission intensity ratios at different Xe contents (total pressure 5 torr).	131
36)	N_2 pressures vs. theoretical emission relationships.	135
37)	Hg- H_2O system.	143
38)	Hg- D_2O system.	144
39)	Emission ratio in Hg- D_2O system.	146
40)	4047A absorption intensity in nitrogen ethane mixtures.	148
41)	4047A absorption intensity in nitrogen propane mixtures.	149
42)	4047A absorption from 0.1% propane- N_2 mixtures.	151
43)	4047A absorption in 0.1% Rh- N_2 mixtures.	153
44)	The quenching of Hg^0 atoms in nitrogen diluted with 0.01% of hydrogen.	154
45)	A schematic reoresentation of $Hg^1 + CO$ potential energy curves.	159

CHAPTER I: INTRODUCTION AND LITERATURE SURVEY

1) Fundamentals of photosensitization

The utilization of energy in chemical reactions is one of the most important factors in the study of reaction mechanisms. By following the distribution and the mode of transfer of energy the reaction mechanism may often be elucidated. In photochemistry, the absorbed light is the source of energy for the excitation. The energy absorbed is readily monitored and controlled. The excitation is usually restricted to certain groups within the absorbing species, so the possibility of fragmentation at other points is considerably restricted.

The nature of chemical changes initiated by the absorption of light depends upon the wavelength (energy) of the incident radiation. The absorption of ultraviolet light ($\lambda < 4000$) leads to the electronic excitation of the absorbing molecule which, subsequently, may undergo chemical changes or relaxation via some photophysical process. The lifetime of the electronically excited molecules may be as short as the period of one vibration of a critical bond, or as long as several minutes or hours. If dissociation is to occur, the energy of the absorbed radiation must exceed the energy of the bond to be broken. This condition is usually

satisfied by the light in the ultraviolet region. If the absorbed energy is greater than that required for the bond to be broken, the fragments must carry the excess energy. These internally or translationally "hot" fragments may trigger secondary reactions.

If the molecule does not absorb light in the appropriate spectral region, photochemical reaction may still be initiated via energy transfer. The electronic excitation energy of an added, strongly absorbing species may be transferred to the substrate, thereby inducing a reaction. This technique is called photosensitization; while the direct decomposition of the absorbing species is known as photolysis.

The technique of photosensitization is not restricted to any particular phase and in principle any atom or molecule can be a photosensitizer. The overall reaction which takes place is dependent upon the conditions of the experiment, and on the nature of the sensitizer used. The simplest photosensitized systems are those taking place in the gas phase involving atoms or simple molecules as sensitizers.

In order to elucidate the nature of a photosensitization system in detail it is necessary to understand the three basic consecutive steps of the process, namely:

- i) the absorption of light by the sensitizer

- ii) the transfer of energy to the substrate
- iii) the chemical and physical changes in the acceptor molecule caused by the transfer of energy.

The choice of an atom or a molecule as a sensitizer depends upon its chemical, physical and spectroscopic characteristics. The excitation characteristics of the sensitizer available electronic states, their energy content, and lifetime can be obtained from spectroscopy. These are important parameters in the understanding of sensitization. It is readily seen then, why atoms or simple molecules are often used as sensitizers, although in recent years a large number of publications have been concerned with the study of the sensitizing actions of large organic molecules. This interest has been stimulated by the role of energy transfer reactions in synthesis and life processes. Fortunately, many principles of energy transfer are common to both atomic and molecular systems, thus the rules derived and elucidated for simple systems can be applied generally in molecular photochemistry.

As well as simplicity, the atom sensitized systems possess additional practical advantages, e.g. high energy content of the excited state, mono-energetic excited species etc. These properties are well exemp-

lified by mercury atoms, and consequently a considerable amount of research has been concerned with the action of mercury as a photosensitizer.

The secondary process, following the absorption of light, is the transfer of energy from the sensitizer to the substrate. In the vapor phase, the transfer is usually the result of collision between donor and acceptor species, but in the condensed phase a number of additional energy transfer modes are possible (e.g. long range interaction, triplet-triplet transfer). Conditions are further complicated in the condensed phase by the importance of various interactions related to reversible complex formation between substrate, solvent and sensitizer molecules, and consequently they become important factors in the interpretation of the mechanism.

In the gas phase, reaction cross sections leading to energy transfer are of the same order of magnitude as gas kinetic collision cross sections. However, even in the vapor phase the available information is insufficient to deduce general relationships, and even simple parameters such as the absolute rate constants for energy transfer are not precisely known for a number of cases.

This thesis discusses the behaviour of the mercury atom as a photosensitizer in the gas phase. It is concerned mainly with the quenching of the lower resonance state, and the role of the lowest excited state, the metastable 3P_0 level in the photosensitization reactions of mercury.

2.a. Mercury as a photosensitizer

The ground state electronic configuration of mercury is $6s^2$ which is designated as 6^1S_0 . If one of the 6s electrons is excited to the 6p level, depending on the orientation of the spin, either singlet or triplet terms result (Figure 1). The absorption of radiation at 1849A will induce a transition to the singlet 6^1P_1 level. The energy of this level is 154 kcal. The triplet terms are 6^3P_2 , 6^3P_1 and 6^3P_0 . It is apparent that the transition to the singlet level is the only one strictly obeying the selection rules. However, due to the high atomic number of the mercury the rule $\Delta S = 0$ is relaxed, thus intercombination of multiplicities is allowed. The selection rule imposed by the change of the $\underline{J}$ vector is obeyed even in this system, therefore neither the $6^1S_0 \rightarrow 6^3P_2$ nor the $6^1S_0 \rightarrow 6^3P_0$ transitions occur. The 6^3P_1 level can be populated by the absorption of 2537A radiation and has an energy of

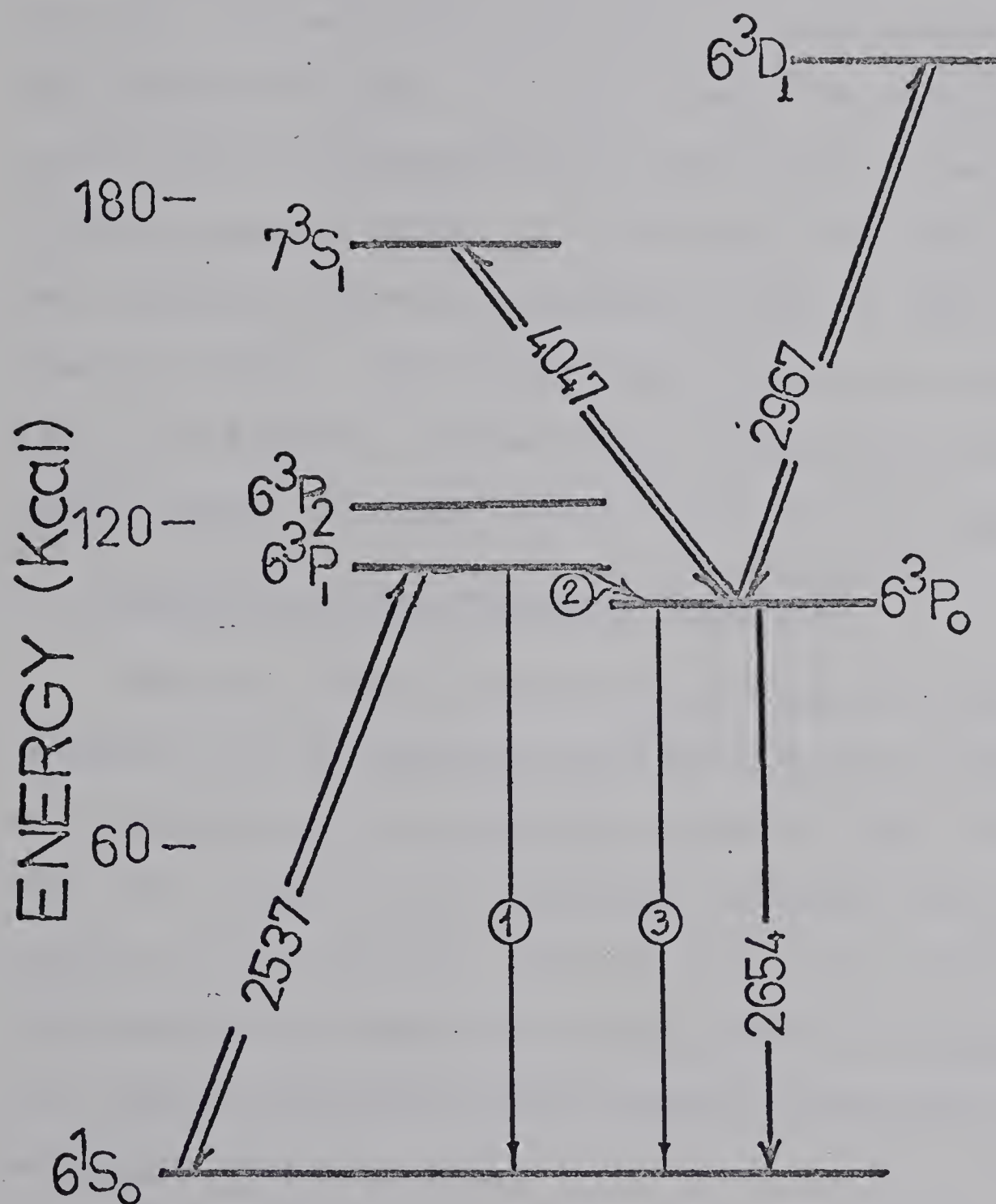


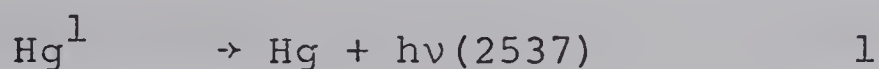
Figure 1. The lower energy levels of Hg atoms.

112 kcal. (the states 3P_1 and 3P_0 will be referred to as Hg^1 and Hg^0 , respectively).

The 3P_2 state is 13 kcal. above the 3P_1 resonance level, thus the collisional activation at room temperature from the 3P_1 to the 3P_2 level is not very probable (one out of every 10^4 collisions has sufficient energy). The metastable level is 5 kcal. below the resonance level and can be populated by collisional relaxation of the resonance state. A relatively weak emission has been observed from the metastable level to the ground state at 2654A. This transition is probably due to the partial relaxation of the $\Delta J=0 \leftarrow + \rightarrow 0$ selection rule in odd atomic weight isotopes having finite nuclear spins (1).

b. Quenching of the resonance radiation.

Wood (2) first noticed the decrease in the intensity of the resonance radiation upon the addition of a foreign gas to a mercury resonance lamp. He attributed this effect to the added gas reducing the concentration of the emitting species. Cario and Franck (3) later showed the decrease is the result of energy transfer from the excited mercury atoms to the added gas molecules. The reactions



were proposed to explain the observation.

The rate of reaction 2 depends on the physical and chemical nature of the quencher molecule. The process described in reaction 2 is commonly referred to as the "quenching of the resonance radiation".

The bimolecular rate constant which is the measure of quenching efficiency, is more frequently expressed in terms of quenching cross section σ_Q^2 . It is related to the rate constant by an analogous expression to that for the gas kinetic collision frequency, (4)

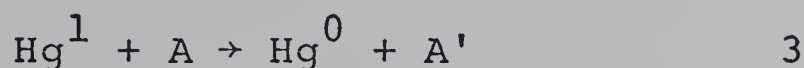
$$k_Q = \sigma_Q^2 \left(8\pi RT \frac{M_A + M_{Hg}}{M_A M_{Hg}} \right)^{\frac{1}{2}} \quad (I-1)$$

where,

M_A, M_{Hg} represent the molecular weights

k_Q the bimolecular rate constant.

The quenching reaction should include a step in addition to reaction 2; namely, the partial quenching to the metastable level (Figure 1).



where A' is an energized molecule.

If the quenching is defined as the decrease of Hg^1 concentration, indicated by the decrease of the resonance phosphorescence, k_Q expresses the combined effects of reactions 2 and 3.

c. The measurement of 3P_1 quenching cross sections.

The methods used to measure quenching cross sections can be classified into two groups. They are the so-called "physical" and "chemical" methods. The physical method is based on the measurement of the change of resonance phosphorescence intensity in the presence of a quenching molecule. This method yields absolute rate constants, while the chemical method yields rates relative to a reference standard.

i. Physical method.

The method is concerned with the competition between reaction (1) and the combined rates of reactions 2 and 3 ($k_{2,3}$). From the steady state approximation we obtain the well-known Stern-Volmer formula (4)

$$\frac{Q}{Q_0} = \frac{1}{1 + \frac{k_{2,3}}{k_1} (A)} \quad (I-2)$$

where,

Q and Q_0 refer to the fluorescence intensity with and without the quencher A respectively.

The evaluation of the constants in this simple equation has been attempted but proved to be not a simple matter.

The ground state mercury atom has a large absorption

coefficient for 2537A radiation, therefore a photon corresponding to this wavelength can be absorbed and re-emitted several times before emerging from the reaction cell. The net effect is a prolonged radiative lifetime for Hg^1 . This phenomenon is known as the "imprisonment of the resonance radiation". It is evident that the imprisonment depends on both the mercury concentration and on the cell geometry. Since the radiation can be quenched as long as it stays in the cell, the rate of quenching is influenced by the time of imprisonment. The Stern-Volmer formula cannot be solved explicitly because of the dependence of k_1 upon the experimental conditions. The approximation of k_1 is an important source of error.

The first attempt to evaluate the imprisonment was made by Zemansky (5). Millne assumed (6) that the radiation transport phenomena can be approximated by a diffusion model and Zemansky applied Millne's theory to calculate k_1 . Millne's assumption that the absorption coefficient is uniform over the line width, which may be expressed as

$$\int K(\nu) d\nu = K\Delta\nu$$

was later shown to be incorrect, since the absorption coefficient is a function of the frequency ν .

Samson suggested (7) the use of an average

instead of a uniform absorption coefficient.

The computation based on the diffusion-model involves a term containing the mean free path, but since the dependence of absorption coefficient on ν prevents an explicit definition of this term, the assumed definition introduces an error to this method.

Holstein treated the problem in a more rigorous manner taking into consideration the spectral line shape, which enabled him to solve the resulting integro-differential equation in an explicit form (8). He showed, that the time of decay for the imprisonment is not only dependent on the cell geometry and the mercury vapour pressure, but also on the spectral line shape of the resonance radiation. He assumed that the line shape is determined mainly by Doppler broadening. The absorption coefficient (k_0) at the centre of the line is

$$k_0 = (2.19 \times 10^{-12} \times N) \times T^{-1/2}$$

where,

N: the number of mercury atoms/cc

T: the absolute temperature

The solution of the transport equation for the imprisonment time (T) is

$$T = \frac{5}{8} k_0 R [\pi \ln(k_0 R)]^{1/2} \quad (I-3)$$

where,

R: the radius of the cell.

T is related to τ , the natural radiative lifetime, by the so-called escape factor g , where $g = \tau/T$.

The correctness of Holstein's theoretical formula was proven experimentally. Alpert, McCoubrey and Holstein (9) found good agreement with the theoretical prediction when $N \leq 1.5 \times 10^{15}$ atoms/cc.

Biberman used the same approach as Holstein (10) except that he applied the steady state treatment for a continuous exciting beam, whereas Holstein employed an exciting beam interrupted by a rotating sector. Biberman's values differ from those of Holstein by a constant factor of 1.23 (see below).

Matland extended Holstein's treatment to calculate quenching rate constants (11). He showed that the decay time in the presence of a quencher becomes

$$\frac{1}{T} = \frac{1}{T_i} + \frac{1}{T_Q} \quad (\text{I-4})$$

where,

T_Q , T_i represent the imprisonment times with and without the quencher respectively.

The quenching cross section can then be calculated from the gas kinetic expression

$$\frac{1}{T} = N \sigma_q \bar{v} \quad (\text{I-5})$$

where,

N : the quenching gas density
 $\bar{v}$: the mean relative speed
 σ_q : the effective quenching cross
 section for a quenching collision.

Matland's value for nitrogen is in satisfactory agreement with the results of Samson (7), Duffendach and Owen (12) which were based on the same Millne-Samson assumptions.

Yarwood, Strausz and Gunning (13) showed that the quenching cross section values obtained by the different methods, differ by constant factors

$$\sigma_I^2 = 1.23 \times \sigma_{II}^2 = 1.23 \times \sigma_{III}^2 = 1.75 \times \sigma_{IV}^2 \quad (I-6)$$

where,

the subscript

I denotes values obtained by Holstein

II denotes values obtained by Zemansky using
 Samson's average absorption coefficient.

III denotes values obtained by Biberman

IV denotes values obtained by Zemansky using
 his original assumption of coherent scattering.

The first three sets of values agree to within 23%. The values of set IV although known to be in error are listed in this thesis because they are frequently quoted in the literature.

K. Yang (14) suggested another approach, also based on the measurement of the resonance phosphorescence in the presence of a quencher. He postulated a linear relation of the following form

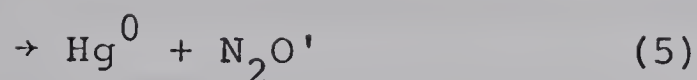
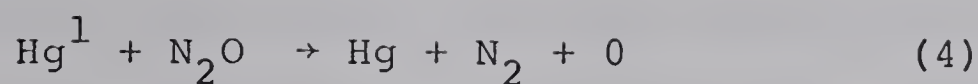
$$\tau k_q = \tau_0 k_q + \text{const.} \times p$$

for the imprisonment lifetime as a function of mercury pressure. Extrapolating to zero pressures of mercury, the imprisonment effect becomes zero and the lifetime becomes equal to τ_0 , the natural lifetime, which can be calculated. He found that the quenching rate constant for ethylene was 12% higher than that obtained by Yarwood, Strausz and Gunning using Holstein's formula (13).

Quenching cross sections and absolute quenching rates, measured by the physical method for various molecules, are listed by Calvert and Pitts (4). The list includes all published values up to 1964. The quenching cross sections for a number of additional molecules have been measured by Yarwood, Strausz and Gunning (13).

ii. The chemical method.

The method, developed by Cvetanovic (15) is based on competitive quenching with nitrous oxide



where,

$\text{N}_2\text{O}'$ denotes an energetic molecule.

Applying the steady state treatment for the competition of reactions 2 and 3 with 4 and 5; we obtain the relationship

$$\frac{1}{\Phi_{\text{N}_2}} = \alpha [1 + \beta \left[\frac{A}{\text{N}_2\text{O}} \right]] \quad (\text{I-8})$$

where,

β : is the slope of the plot $1/\Phi_{\text{N}_2}$ vs. $A/(\text{N}_2\text{O})$ divided by the intercept.

α : the intercept

Φ_{N_2} : the quantum yield of N_2 .

β is related to the quenching cross section by the expression

$$\frac{\sigma_{\text{A}_0}^2}{\sigma_{\text{A}}^2} = \beta \left(\frac{1 + M_{\text{Hg}}/M_{\text{A}}}{1 + M_{\text{Hg}}/M_{\text{A}_0}} \right) \quad (\text{I-9})$$

where,

A_0 : refers to the reference standard

M : the respective molecular weights.

The fundamental requirement for this method is the absence of a source of N_2 other than reaction (4).

Cvetanovic also pointed out that the presence of oxygen atoms can result in the formation of a solid deposit with mercury, Hg^0 causing self-inhibition of the process. Therefore reaction it is desirable to remove the oxygen atoms from the system by a scavenger.

Yang (16) examined the possible interference from the reaction

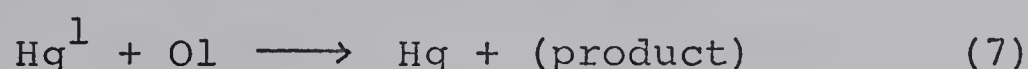


which is important only in hydrogen. His conclusion was in agreement with that of Cvetanovic, that for reproducible results the addition of a hydrogen atom consuming compound (eg. an olefin) is necessary. The rate equation then becomes

$$\frac{1}{\phi_{\text{N}_2}} = 1 + \frac{k_4(\text{A})}{k_2(\text{N}_2\text{O})} + \frac{k_7(\text{Ol})}{k_2(\text{N}_2\text{O})}$$

where,

k_7 is the rate constant for the reaction



The review by Cvetanovic (15) contains all the quenching cross sections measured by the chemical method up to 1964. Additional values were reported by Bellas, Rousseau, Strausz and Gunning (17). These authors concluded from their results that a serious

discrepancy exists between the physical and chemical quenching measurement, and that the resulting values do not always agree as previously assumed.

d. The partial quenching of Hg^1 state.

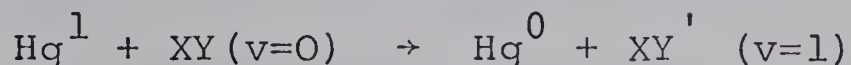
A particular mode of removal of Hg^1 atoms is collisional deactivation to the metastable level. Since this transfer involves only 5 kcal. and not the total excitation energy of 112 kcal., the process can be regarded as a partial quenching process. The role of Hg^0 atoms in the mercury photosensitization has been the subject of a great deal of speculation. For example, Strausz and Gunning (18) showed that addition of nitrogen to CO_2 undergoing photosensitization increases to decomposition yields. The effect was attributed to the intervention of Hg^0 atoms.

The 5 kcal. energy involved in the transfer is insufficient to induce any electronic excitation, consequently it has to appear as translational, rotational, or vibrational energy of the acceptor. The conversion of electronic to translational energy is a somewhat inefficient process, therefore atoms which have only translational freedom will be quite effective in bringing about this transition.

That Hg^0 has negligible importance in photosensitization (19) is a good assumption in many cases. However, for example in nitrogen, where Hg^0 is present

in high concentration the predominant, if not the only mode of quenching is to the metastable level.

A quantum mechanical treatment of the process



was carried out by Nikitin and Bykhovskii (20). They concluded that the most probable result would be a vibrational excitation of the diatomic species XY. The rate constant for nitrogen showed reasonable agreement with observation. They predicted the same quenching efficiency for CO and N₂ by this process. The temperature effect was predicted to be greater than the observed value, which suggests some inadequacy in their theoretical model.

Later Karl and Polanyi succeeded in detecting vibrationally excited CO and NO molecules by IR emission spectroscopy in mercury photosensitization (21,22), thus verifying Nikitin and Bykhovskii predictions.

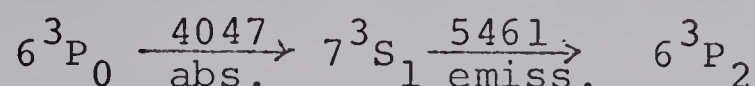
The observation of Hg⁰ in pure mercury vapor suggests that atoms initiate an electronic to translational energy conversion. This process appears to take place readily at high concentrations of mercury and at elevated temperatures (23).

e. The detection of Hg⁰ atoms.

The first direct method of observing Hg⁰ was described by Wood (24) in 1924, and slightly improved by Pool a few years later (25). The technique was further improved by Kimbell and LeRoy (26). The method is based on the absorption of the 4047A light, corres-

ponding to the transition $6^3P_0 \rightarrow 7^3S_1$.

Asada et al (27) used a method based on the following absorption-emission sequence



They monitored the 5461A emission intensity, which is related to the concentration of the metastable atoms.

I. Popescu et al (28) confirmed both Wood's and Asada's results. Their light beams contained the 2537 and 4047A components and thus populated the 7^3S_1 level directly. At right angles to this beam path, they observed, with a photomultiplier, the emissions originating from this level. Emissions at 4047, 5461 and 4358A were isolated by means of a monochromator. The 4358A emission corresponds to the transition $6^3P_1 \leftarrow 7^3S_1$.

Berberet and Clark's (29) arrangement was essentially the same as Popescu's. They measured the emission intensities originating from the decomposition of the excited mercury molecule and the effect of nitrogen on the concentration of Hg^0 atoms. They found that the 4047A light was absorbed according to Beer's law and that at high irradiation intensities a significant fraction of the mercury atoms can occupy the metastable level. They did not find evidence for a third body induced emission, which had been suggested as the origin of one of the emission bands of the excimer in pure

mercury vapor (23). The formation of a molecular ion Hg_2^+ was suggested to be due to the collision of $^3\text{P}_0$ and $^3\text{P}_1$ atoms followed by a subsequent ionization.

The effect of nitrogen on the resonance phosphorescence has been extensively investigated, at room temperature. Although nitrogen reduces the emission intensity heating decreased the effect of nitrogen. This observation suggests that N_2 does not quench Hg^1 nor Hg^0 atoms to the ground state (30). Bignon and Cojan (31) suggested that N_2 removes Hg^0 atoms mainly by collisional reactivation to Hg^1 level.

Another method for detecting Hg^0 atoms was described by Couliette (32), and later further exploited by Darwent and Hurtibise (33), is based on electron emission from a metal plate upon the impact of metastable atoms. The current is a measure of the metastable atom concentration. Darwent and Hurtibise reported quenching to the metastable level by C_2H_4 , C_2H_6 , H_2 and several other gases. These compounds had not been previously observed to quench to the metastable level and it suggested that Darwent and Hurtibise's observations

were in error. The formation of the molecular ion, Hg_2^+ , the dependence of work function on the gas present, and the absorption of gas on the plate were suggested as possible sources of error (30).

Sheer and Fine (34) used this method in their study of relative quenching efficiencies of CO and N_2 . They found silver to be a satisfactory cathode material. It had similar responses for both gases. They examined Zemansky's proposal that the observed quenching efficiency ratio $\sigma_{\text{CO}}^2 / \sigma_{\text{N}_2}^2 \approx 20$ is related to the increased quenching rate by CO to the metastable level. However they found that the quenching rates to the metastable level for CO and N_2 were almost equal. They concluded that the higher quenching efficiency of CO was due to a larger quenching rate for Hg^1 atoms deactivating directly to the ground state. This quenching cross section is near zero in nitrogen. Since their objective was to determine relative rates, the error in the absolute measurement should not alter their conclusion.

A different technique, that of flash photolysis, was used by Callear and Norrish (30) to determine Hg^0 atom reactivities. Their method consisted of the following steps:

- i. A high intensity short duration photolytic flash produces a high concentration Hg^1 atoms which are deactivated to Hg^0 with 1 atm. of N_2 ,
- ii. $^3\text{P}_0$ atoms are detected and their concentrations monitored by kinetic absorbiometry of the $2967\overset{\circ}{\text{A}}$ line corresponding to the transition $^3\text{P}_0 \rightarrow ^3\text{D}_1$.
- iii. the change of absorption intensity in the presence of an added gas (to N_2) is related to their reactivity with respect to Hg^0 atoms.

Callear and Williams were able to measure quenching cross sections for Hg^0 by this technique (35).

The disadvantage of the method is the relatively high pressure required and the difficulty of controlling the temperature. The measurements are of questionable validity with compounds which emit in the spectral region of the absorption measurement.

f. The removal of Hg^0 atoms.

The rate of Hg^0 atom formation must be equal to its rate of disappearance in the steady state. Hg^0 may decay by the following routes;

- i. The emission of the forbidden line, 2654A.
- ii. Deactivation on the wall; reactivation to the Hg^1 level via energetic collisions
- iii. Quenching by the substrate
- iv. Quenching by ground state mercury atoms.
- i. The emission of the forbidden line, 2654A.

The appearance of the 2654A line in the mercury emission spectrum, the so-called "forbidden" line, is the result of the transition $6^1\text{S}_0 \leftarrow 6^3\text{P}_0$.

The term "forbidden" refers to a low transition probability. The selection rules which govern the probability of a particular transition are applicable to varying degrees for different atoms, depending on the validity of the assumptions made in the derivation. The selection rule $\Delta J \neq 0$ when $0 \rightarrow 0$ transition occurs is not strictly obeyed in atoms with finite nuclear spin. The odd isotopes of mercury all possess finite nuclear spins which couple with J hence the resulting vector will not be zero. Consequently the 2654A line appears weak in the mercury emission spectrum (36).

Kimbell and LeRoy (37) showed that a rapid energy exchange must occur between even and odd

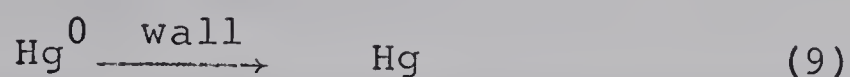
atomic weight isotopes. Thus the radiation from a mono-isotopic lamp, containing only ^{199}Jg did not result in any increase of the forbidden line intensity. This is due to rapid energy exchange between the excited odd and the ground state even isotopes.

The same authors have reported a detailed study of the kinetics of the $2654\text{\AA}^{\text{O}}$ emission. The emission intensity was found to increase with increasing nitrogen pressure to a maximum at 9 torr N_2 above which it became pressure independent. The steady state concentration of the Hg^{O} atoms, however, exhibited a different pressure dependence. It increased with increasing N_2 pressure up to ~ 9 torr above which it gradually decreases. If the effect is real, it would seem to indicate a pressure dependence of the forbidden emission intensity.

ii. Deactivation on the wall; reactivation to the Hg^{I} level via energetic collisions.

There are few discussions of these decay process in the literature.

Kimbell and LeRoy (26) considered diffusion to the wall



as a mode of decay for Hg^0 atoms. They solved the differential equation describing the diffusion transport in a nitrogen filled, uniformly irradiated, cylindrical reaction cell.

The rate constant is given by the expression

$$k_9 = \frac{4D^0 N_2}{R^2} \quad (\text{I-11})$$

where,

R: the radius of the reaction cell, and

D^0 : the diffusion coefficient.

The value of D^0 was not available for Hg^0 , therefore they used that given by Spier (38) for Hg. They calculated k_9 to be 206 mm sec^{-1} .

Bigeon and Cojan (39) concluded that this process can account for about 50% of the destruction of Hg^0 atoms at room temperature and at 2 mm pressure of nitrogen in a cell of 6 mm radius.

There is even less information available on the reactivation of Hg^0 to Hg^1 .

It is known that this process takes place in nitrogen-mercury mixtures at high temperatures (30).

Bigeon and Cojan, in another communication suggested (31) an appreciable rate for this reaction even at room temperature in nitrogen, since $\text{N}_2(v=1)$ can either deactivate on the wall or induce the transition $^3\text{P}_0 \rightarrow ^3\text{P}_1$. This latter process would be favored since the chance of collision is 24 times greater than for deactivation on the wall. However this suggestion ignores the fact that the collisional relaxation of the vibrationally excited molecule is very rapid (40), thus it is more favorable than the activation of $^3\text{P}_0$ atoms. Very little is known about the efficiency of vibrational-electronic energy transfer, although it was reported to be efficient at elevated temperatures (23).

The translational-electronic energy transfer in Hg^1 quenching could be important in thermally induced reactivation although little is known about the system.

iii. Quenching by the substrate.

Only a few publications have appeared so far dealing with this aspect of the decay (35). The paper

by Callear and Williams is a refinement of the first communication by Callear and Norrish (30). They showed higher reactivities for Hg^1 than for Hg^0 atoms in every gas they examined. The quenching cross sections obtained for the two different excited species did not show any apparent relation to one another.

Polanyi et al studied the vibrational excitation of CO (21) and NO (22) on collision with both Hg^1 and Hg^0 atoms. They concluded that Hg^0 can initiate this excitation, but about 10 times less efficiently than Hg^1 . Callear and Williams (35) found the reactivity ratios for the energy transfer efficiencies of CO and NO to be 150 and 75 respectively.

iv. Quenching by the ground state mercury atoms.

There is general agreement that the reaction of Hg with Hg^0 in the presence of a third body is a major mode of decay for the metastable atoms.

Franck and Grotrian suggested the formation of a molecule (41). About 10 years later Lord Rayleigh (42) concluded that the formation always takes place in the presence of metastable atoms. The first thorough investigation of the formation and decay of this molecule was carried out by Mzorowski. He reviewed the earlier work, and in a number of papers published his own observations (43). His work can be summarized

in the following way:

1. There are two possible excited electronic states available within the energy range of the system, the $^3O_u^-$ and the 3l_u states, the former lying below the latter, both being (j/j) coupled.
2. At short internuclear distances the two states converge into the common (l,s coupling) $^3\Sigma_u^-$ state.
3. The reaction giving rise to the excimer is

$$Hg^0 + Hg \xrightarrow{M} Hg_2 (^3O_u^-)$$
4. Both states can decay via emission. The so-called "a" band which has a maximum at 4850Å, originates from $^3\Sigma_u^-$; while the "b" band originates from the 3l_u state and has a maximum at 3350Å.
5. Upon heating, the intensity of the "b" band decreases and that of the "a" band increases.
6. Both bands decay simultaneously.

Mzorowski's interpretation of the two states was criticized by McCoubrey (23). He suggested that both bands originate from a common electronic state, one by a spontaneous, and the other by a pressure induced, trans-

ition to the ground state. His criticism is based on the parallel decay of the two emission bands, suggesting a common emitting species. The ratio of $I(a)/I(b)$ showed a second order dependence on pressure. Both Mzorowski and McCoubrey carried out their studies in a pure mercury system.

Berberet and Clark (29) studied the formation and the decay of the excimer in nitrogen. They reported a low intensity for the "b" band relative to the "a" band, which was intense and showed a linear dependence on nitrogen pressure above 8 mm.

Callear and Norrish (30), and later McAlduff and LeRoy (44), postulated the formation of some kind of molecular species in their mechanism for the decay of Hg^0 atoms. LeRoy et al (45) could detect a very weak emission in the "a" band region, only when N_2 was added, but could not see the "b" band. There is little doubt that "b" band emission exists and their failure to observe this was probably due to an insensitive detection device.

3. Correlation of energy transfer efficiencies with the molecular parameters of the acceptor molecule.

The large volume of publications concerned with energy transfer processes cannot be reviewed within the

scope of this thesis. Literature containing pertinent information to mercury photosensitization will be considered, particularly where they relate directly to energy transfer efficiencies in the gas phase.

As previously mentioned, the principal mode of energy transfer in the gas phase is by collision. The efficiency of the process is customarily expressed by collision cross section based on gas kinetic theory.

Magee and Ri (46) and Laidler (47) have used potential energy surface calculations to obtain values for quenching radii. They attempted to correlate the collision radii to the ionization potential, the excitation energy of the sensitizer and the electronegativity of the quencher. The theory is only of a crude approximation and is inadequate for general application.

Bellas et al (17) attempted to show a correlation between group electronegativity and quenching cross sections. The lack of electro-negativity values allowed them to make only a limited number of comparisons. Their results show that such a correlation does exist for the available data.

It was obvious from the comparison of quenching cross section values that the excited sensitizer atom

exhibits a certain selectivity in the energy transfer process. The collision is the most efficient when two major rules are satisfied

- a) spin conservation
- b) resonance energy rule

The first rule simple states that the total spin before and after collision remains unchanged. Although this rule is violated in some cases, it is generally obeyed in atomic systems (48).

The resonance energy rule requires that the minimum amount of energy be converted into translational motion. This rule is invariably obeyed in atomic systems. However, as pointed out by Kondratiev and Siskin (49) it is frequently violated in molecular systems due to accidental resonance, therefore the explanation of quenching cross section would be very complex in terms of energy resonance. The rule is often omitted from the discussion of energy transfer involving molecules.

This implies that the excited atom must be considered not only as an energy carrier, but also as a chemical species which can preferentially interact with certain molecules.

Rousseau, Gunning and Strausz (50) concluded from reactivity studies of oxygen, sulphur and Hg^1 atoms with olefins, that the excited mercury atom

has an electrophilic character. The efficiency of the energy transfer is very high in the presence of a C-C π orbital. The transfer is thought to promote a triplet π - π^* transition in the olefin. The quenching cross section showed a systematic variation with structural changes in the olefin which could be correlated with the electrophilic character of the attack (to form an activated complex (19)). Increasing alkyl substitution on the doubly bonded carbon increases the reactivity of the π -bond, as was found for other electrophilic reagents such as triplet oxygen, sulfur and selenium atoms etc., while substitution of electron withdrawing groups decreases the reactivity. They also drew attention to the fact that Darwent's empirical relation (19) of specific increments for methyl methylene and tertiary C-H groups in quenching was related to their electron donating power. However, the replacement or the addition of these groups does not always result in the predicted change, since other factors pertinent to quenching may also change upon substitution (eg. steric hindrance, orbital overlap).

Rousseau, Woodall and Gunning (51) reported the observation of a decrease of the quenching cross section upon substitution of certain hydrogens with deuterium. They found the largest decrease occurred when secondary and tertiary hydrogens were replaced, indicating that

these are the most important quenching sites in saturated hydrocarbons.

It is obvious that the colliding species must spend some time in intimate contact during which the energy is transferred. The contact time can be very short or infinitely long. In the latter case the collision leads to the formation of a stable compound. If the donor-acceptor association is sufficiently long for the pair to perform a few vibrations, the term "reaction intermediate" or "transition complex" is used. "Excited intermediate" usually refers to a donor-acceptor association pair in which the donor energy still resides in the complex.

In the mercury photosensitized system the excited intermediate may involve either Hg^1 or Hg^0 atoms, and one or more substrate molecules. The donor excitation energy is converted to some form of potential energy, or causes chemical reaction or is released as fluorescence. The relative importance of these alternatives determines the quantum yield of decomposition.

The observation of the low quantum yield in methane decomposition led Back and Auwera (52) to suggest that there must be a competing process which

they called "quenching without decomposition". The suggestion was speculative and they did not attempt to detect emission as a possible competing process.

Later Back and Takamuku (53) attempted to explain the low decomposition yields for ammonia and ammonia-propane mixtures on the same basis. The emission from ammonia-mercury and water-mercury mixtures were observed some 34 years earlier by Gaviola and Wood(54). They assigned the emission bands in both cases to the formation of an excited intermediate involving Hg^1 atoms. The emission extended from 2900 to 4000Å and from 2537 to 3120Å with ammonia and water respectively. Although they have shown that the emission is directly related to the presence of Hg^1 and not Hg^0 atoms, it was not certain if the association of products or the substrate with excited mercury was the source of emission.

Oldenberg (55) and Kuhn and Oldenberg (56) reported the appearance of a diffuse, moderately strong emission band from the mercury-noble gas mixtures. In this case no chemical reaction occurred, and there was no doubt that the emission originated from the noble gas-mercury intermediate.

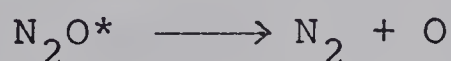
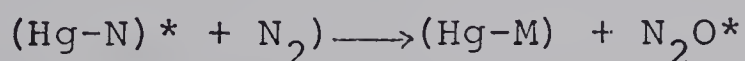
Glocker and Martin (57) described similar behaviour

for methane-mercury mixtures. Their experimental arrangement was not well suited to detailed spectral studies, nevertheless they were able to detect a feeble emission band around 2575Å. This is clearly one mode of energy dissipation from the system, in agreement with the findings of Back and Auwera (52), who were apparently unaware of the earlier study of Glocker and Martin. Nevertheless the anomalous behaviour of methane reaction could not be fully explained by the emission.

Homer and Lossing (58) obtained chemical evidence for the formation of $(\text{HgCO})^*$ as an excited intermediate in the mercury sensitization of ethylene. They have also showed that the reactive species involved in the complex formation is the Hg^1 and not the Hg^0 atom.

The recent work of Polanyi et al (21) lends additional support to this proposal of complex formation, but their experimental evidence indicates that Hg^0 atoms could also contribute to its formation. They found that the metastable atom reactivity in complex formation is about one tenth of that of Hg^1 . In a later paper (22) the same authors reported the formation of a similar complex involving NO. The decomposition of the excited intermediate resulted in the formation of a vibrationally excited molecule, detected by IR emission spectroscopy.

During the preparation of this thesis, K. Yang published a paper (59) on the energy transfer mechanism in mercury photosensitization. He relied heavily on the two preliminary publications from the material of the present thesis which appeared in J. Chem. Phys., 43, 4524-26 (1965), *ibid* 45, 2322-23 (1966), for quenching based on the symmetry properties of the intermediate complex. With the exception of propane his quenching cross section values differ by a constant factor from those previously published (see Appendix). He found, $\sigma_{\text{chem}}^2 > \sigma_{\text{phys}}^2$ for propane, while the opposite $\sigma_{\text{chem}}^2 < \sigma_{\text{phys}}^2$ was reported previously. He noted an excessive nitrogen formation from propane-N₂O mixtures, and since no Hg⁰ atom presence was reported in this system he suggested alternative reactions, such as



These reactions can take place only when the intermediate lifetime is sufficiently long for collision with N₂O. It was shown, that in propane (Hg-M)* cannot be deactivated by the substrate pressures up to 500 torr, suggesting a short lifetime, hence the origin of nitrogen in propane N₂O mixtures is unlikely to result from the above reaction sequence. Yang developed a

theory to explain the previously reported low quenching of Hg^0 by H_2 compared to that of paraffins. The opposite of this observation was proven experimentally (Figure 44). He found similar temperature effect on the quenching rate of propane and propane d_2 , and hence proposed that the isotope effect must originate from a source other than the change in zero point energy. According to his arguments based on phase space theory the isotope effect may be related to the difference in rotational spacing of the C-D and C-H bonds. This conclusion implies that the collisional relaxation results in the formation of a rotationally excited molecule rather than the previously suggested vibrational excitation (19, 20). There is no experimental data available at present to support either suggestion. He attempted to explain Hg^1 to Hg^0 quenching in terms of the phase space theory of reactions rates.

The kinetic isotope effect may be explained in terms of

- (a) an activation energy effect due to a difference in zero point energy
- (b) phase space theory (60)
- (c) the effect of vibrational wave functions on the transition probabilities between electronic energy surfaces (61).

Theory (a) is based on the assumption that the quenching process has an activation energy. Indications from recent data suggest that the process does have a small activation energy (59). Theory (b) has been described above. Theory (c) was proposed by Robinson et al (61) and it was used to explain the longer phosphorescence lifetime of deuterated, as compared to protonated compounds.

The transition has high probability when the distribution maximum of the vibrational levels of both states appear at the same internuclear distance (i.e. maximum overlap of the vibrational wave functions. Since deuteration changes the vibrational spacing, the result will be a decrease of transition probability, i.e. a lower emission intensity.

From the above review of previous work on energy transfer mechanism in Hg photosensitization it can be seen that the detailed mechanism is the subject of some speculation. The basic questions considered in this thesis are:

- (i) What is the nature of the activated complex for energy transfer?
- (ii) What are the molecular parameters affecting the efficiency of the process?
- (iii) What is the role of Hg^3P_0 atoms in triplet mercury photosensitization?

CHAPTER II. EXPERIMENTAL

1) The measurement of 3P_1 quenching by the physical method.

i. Principle

In the physical method, quenching is measured by the change of resonance phosphorescence intensity upon the addition of a foreign gas to mercury vapour. The change is related to the concentration of the emitting Hg^1 atoms regardless of the way in which it is removed from the resonance level. Hence the quenching rate constant, obtained by the physical method is a measure of all modes of decay initiated by the quencher.

Equation I-2 relates the quenching function to the concentration of the quencher. The lifetime of Hg^1 atoms is $1/k_1$; the quenching rate constant is k_Q . Eq. I-2 can be re-arranged to

$$\left(\frac{1}{Q} - 1\right) = \tau k_Q p_{(A)} \quad \text{II-1}$$

The slope of the plot $[(1/Q)-1]$ vs $p_{(A)}$ is a measure of the quenching rate and hence the quenching cross section. The relationship between these two quantities is described by Eq. I-2.

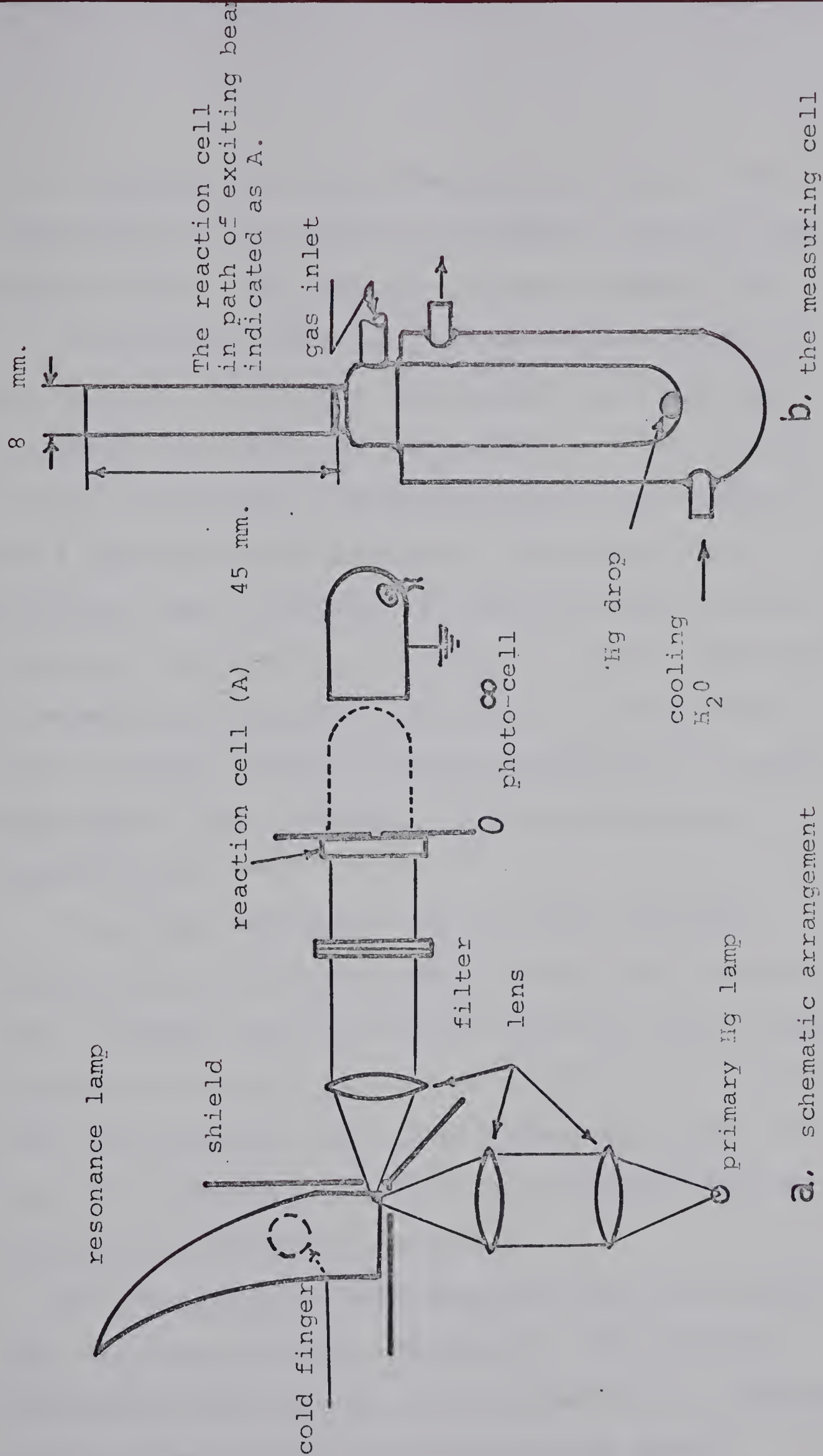
ii. Description of the apparatus

The vacuum system used had a conventional pumping system, storage area and distillation train. Grease free, mercury float, or Hoke Type valves were used. The system was evacuated to $<10^{-6}$ torr prior to introducing the experimental gas to the reaction cell.

A pyrex spiral connected the vacuum system to the reaction cell. It allowed approximately 4 cm. horizontal displacement for the cell. This arrangement was necessary for those measurements in which the light was required to enter the photocell without passing through the reaction cell. The cell (Figure 3.b) was of similar shape and dimension to that of Zemansky's (5). The mercury droplet was kept at 20°C providing a pressure of 1.2×10^{-3} torr.

The overall arrangement for the fluorescence measurement is shown in Figure 2.a.

The primary light source was a laboratory built DC operated low pressure resonance lamp made of Vycor. A cooling jacket, made from the same material, surrounded the lamp. It had two separate compartments. The lower, surrounding the electrode pools, was kept at 40°C , while the upper part enclosing the emitting area was kept at 35°C . The cooling waters



The experimental arrangements and the measuring cell for Fig 1 quenching cross section measurement.

were controlled by Colora Thermostatic baths. The temperature of the outflow was within $\pm 0.1^{\circ}\text{C}$ of the desired value. The lamp drew 6 Amp. at about 175V.

The primary light was collimated and focused on the entrance window of a horn-shaped resonance lamp. The 2537A exciting light was emitted at right angles to the primary beam. Both beams were taken through small apertures placed close to the edge of the resonance lamp. The mercury vapour pressure in the resonance lamp was kept constant by a small cold finger attached to the bottom of the lamp. It contained a drop of triple distilled mercury cooled by ice water. This type of lamp produces a sharp, non-reversed emission line.

The light emitted by the resonance lamp was collimated by a lens and passed through the reaction cell. Between the lens and the reaction cell a frame, permitted a shutter, or slit or a filter to be placed into the beam path. The filter served to correct for the light intensity variation; its operation will be discussed in the following section.

The intensity of light emerging from the reaction cell was measured with a photocell. The photocell electrodes consisted of a platinum mesh and a platinum plate enclosed within a hydrogen filled quartz envelope. A blackened aluminium housing provided

shielding from scattered light and from electrical interference. The photocell was either close to the back of the reaction cell or 10 cm. away. At the furthest point, regarded as being at infinite distance, the unabsorbed collimated beam only was recorded, but at "zero" distance the scattered light was also recorded. The difference in photocurrents is proportional to the resonance phosphorescence which appears as scattered radiation.

The photocell was connected to a pre-amplifier, which compensated for the photocell dark current and improved the matching of the impedance to the recording system.

The connection to the Jarrell Ash Electronic Recording system, was via a shielded cable. The arrangement assured virtually interference-free operation.

The relative positions of the primary light source, the collimating lenses were rigidly mounted in their predetermined positions. They were at right angles to the optical bench supporting the resonance lamp, the filter, reaction cell and the photocell. This arrangement was required to assure reproducible positioning for the photocell and reaction cell.

The photocurrent ratio at "zero" and at "infinite" distance did not change to any appreciable extent after several months of operation, consequently it was unnecessary to determine the light intensity at infinite distance for each experiment.

iii. Calibration and general operating conditions.

The materials used were always of the highest available purity, and where necessary they were purified until no impurities were detectable with V.P.C. or mass spectrometry. Pressure measurements were made with a McLeod gauge.

The "warming up" time was at least 2 hours for the electronic units, and approximately 10 - 15 minutes for the primary light source. The cold finger of the resonance lamp was placed into ice water at least 5 hours before a measurement was made. When possible it was immersed over night in ice water to assure liquid-vapour equilibrium.

The thermostatically controlled sections, heated or cooled, were maintained to within $\pm 0.1^{\circ}\text{C}$ of the desired temperature. The room was air conditioned, at 20°C . A maximum $\pm 1^{\circ}\text{C}$ variation in room temperature was noted.

The quenching function (Q) is defined as the ratio of the resonance phosphorescence intensity in the presence of a quencher to that in its absence,

$$Q = \frac{I_0(p) - I_\infty(p)}{I_0(v) - I_\infty(v)} \quad \text{II-2}$$

where,

I_0 , I_∞ , represent the photocurrents at "zero" and "infinite" distance; subscripts, p: the presence of a quencher at p pressure, v: the evacuated cell.

The I_∞ values are the same, since the absorption is not affected by the presence of the quencher.

Furthermore, $I_\infty(v)/I_0(v)$ is a characteristic of the experimental arrangement, denoted by α . Substituting and re-arranging Eq. II-2

$$Q = \frac{1}{1 - \alpha} \left(\frac{I_0(p)}{I_0(v)} - \alpha \right) \quad \text{II-3}$$

It was found that $I_0(v)$ drifted slowly during the measurement, so a simultaneous determination with $I_0(p)$ was necessary.

It was not possible to do this directly since the preparation of the cell for the measurement required

approximately 1 hour. This difficulty was overcome with the use of the filter. First an $I_{0(v)}$ measurement was made. The reaction cell was then removed, the filter placed into the beam and the light intensity (K) was recorded again. The ratio $I_{0(v)}/K$ is a constant (B), independent of the variation of the light intensity. Since K can be determined immediately before and after $I_{0(p)}$, Eq. II-3 can be rewritten

$$Q = \frac{1}{1 - \alpha} \left(\frac{I_{0(p)}}{KB} - \alpha \right) \quad \text{II-4}$$

Each recording was taken over 150 sec. and the base line recorded for 30 sec. on each occasion. The total time requirement for the set of measurements was 570sec. If the change of K exceeded 3.5% between the values obtained before and after $I_{0(p)}$ was recorded, the observation was discarded and repeated with fresh gas.

The exact duplication of cell position was important for comparison of the measurements. The reaction cell was made to slide in and out of the beam between two wooden blocks, the matching of marks on the stationary and moving parts enabling reproducible positioning.

Calibration was carried out with hydrogen and oxygen. The relationships obtained by Zemansky for these two gases were

$$\tau k_{Q(H_2)} = 1.167p_{(H_2)} \quad \text{II-5a}$$

$$\tau k_{Q(O_2)} = 0.694p_{(O_2)} \quad \text{II-5b}$$

The values of $(1/Q) - 1$ are listed for hydrogen and oxygen at different pressures in Table 1. The least mean squares treatment, with the line passing through the origin yields

$$\frac{1}{Q_{(H_2)}} - 1 = 6.67p_{(H_2)} \quad \text{II-6a}$$

$$\frac{1}{Q_{(O_2)}} - 1 = 4.02p_{(O_2)} \quad \text{II-6b}$$

Combining the appropriate pairs of Eq. II-5 and II-6, we obtain

$$\tau k_{Q(H_2)} = 0.175\left(\frac{1}{Q} - 1\right) \quad \text{II-7a}$$

$$\tau k_{Q(O_2)} = 0.173\left(\frac{1}{Q} - 1\right) \quad \text{II-7b}$$

TABLE 1

Relationship between pressure and quenching of calibrating
gases

<u>Hydrogen</u>		<u>Oxygen</u>	
P [mm]	1/Q-1	P [mm]	1/Q-1
0.042	0.249	0.054	0.213
0.063	0.421	0.073	0.296
0.082	0.562	0.078	0.286
0.099	0.682	0.112	0.429
0.129	0.818	0.190	0.830
0.145	0.988	0.202	0.810
		0.245	0.947

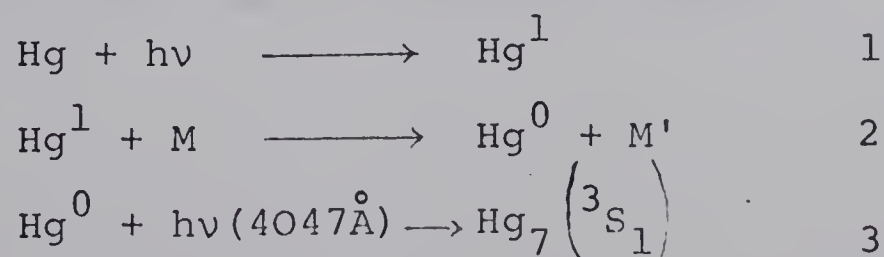
The mean value of 0.174 was adopted for the calibration factor. A value of 0.156 was obtained by Yarwood, Gunning and Strausz (13).

Inconsistent values for the quenching cross section values have been reported in the literature. The theoretical interpretation of the parameters involved is chiefly responsible for these discrepancies, but the experimental conditions are also in part responsible. Therefore well-defined experimental conditions were used. The experiments attempted to measure quenching rates under conditions similar to those of Zemansky, thus the newly obtained values will be directly comparable to those most frequently quoted in the literature. This explains the reason for using a photocell instead of the more sensitive, recently developed photomultiplier.

2. The measurement of 3P_0 concentration by the 4047Å absorption technique.

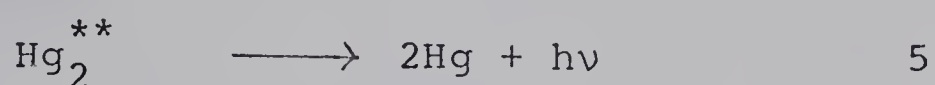
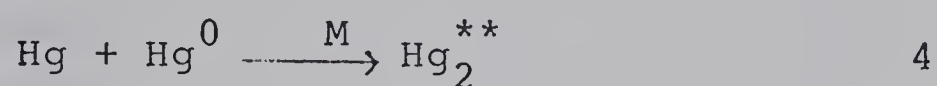
i. Principle

The principle used in the present work of Hg^0 detection was first described by Wood (24). It is based on the following scheme



The change in transmission of $4047\text{\AA}$ light intensity is related to Hg^0 atom concentration.

The apparatus used for Hg^0 determination can also be applied to the detection of Hg_2^* . The decay of the excimer was followed by monitoring the intensity of the two emission bands, the "a" band at $4850\text{\AA}$ and the "b" band at $3350\text{\AA}$, suggested to originate from the reactions

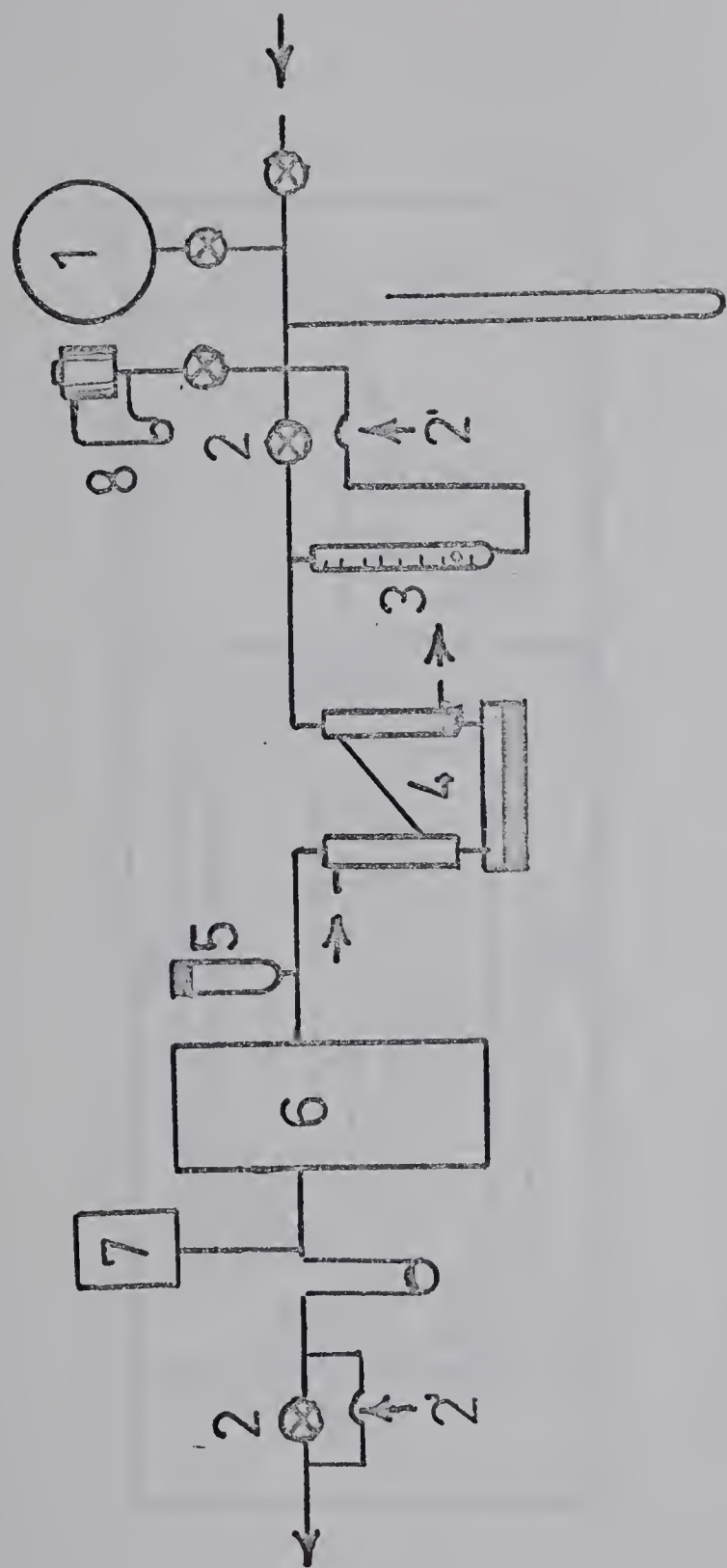


where,

$h\nu(a)$, $h\nu(b)$, represent the emission bands having maximum intensities at 4850 and at $3350\text{\AA}$ respectively.

ii. Description of the apparatus.

The vacuum system was of a conventional design, and the manipulation of gases followed standard practice. The measurements were carried out in a flow system which provided for a constant flow of gas, or gas mixtures, saturated with mercury vapour through an illuminated zone. A schematic diagram is shown in Figure 3 and further details of the cell unit in Figure 4.



1. STORAGE BULB

2. FLOW AND PRESSURE ADJUSTING VALVES

3. ROTAMETER

4. Hg SATURATOR AT 20°C

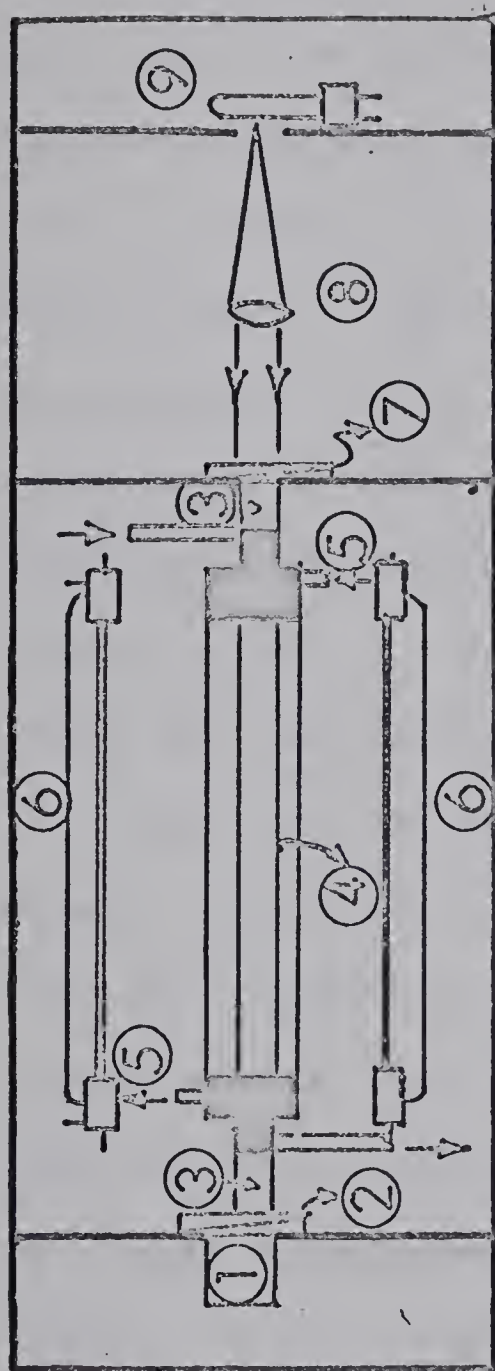
5. PIRANI FUSE

6. FLUORESCENCE CELL UNIT

7. ATLAS MMCF VACUUM GAUGE (OUTPUT TO X-AXIS OF X-Y PLOTTER)

8. MIXING UNIT

Fig. 3 Experimental arrangements for the study of 40f7A absorption and emissions from Hg_2^* .



- (1) Photomultiplier
- (2) Interference filter
- (3) Connecting tubes
- (4) Reaction cell
- (5) Filter-soluted Hg resonance lamps for production of Hg^3P_1
- (6) Watercooled Hg resonance lamps
- (7) Pyrex filter
- (8) Quartz collimating lens
- (9) Monitoring beam source

Figure 4. The cell unit for 4047A absorption measurement.

The substrates were degassed after introduction to the system. If their purity was of doubtful quality, samples were taken and analysed by NMR or mass spectrometry. Each run was carried out using fresh gas from the storage bulb. When hydrocarbon-nitrogen mixtures were used, the mixing was carried out in a vessel fitted with a glass magnetically driven mixer. The gas flow was saturated with mercury by passing it over a heated mercury surface. Reflux condensers on both sides of the saturator were supplied with thermostatically cooled water; its temperature was 20°C, corresponding to a vapour pressure of 1.2×10^{-3} torr. All valves were grease free.

The flow was regulated with Edwards needle valves, and measured with a rotameter. The pumping rate was regulated with a valve, and as a result a slow pressure 'build-up' took place in the cell. The flow was not a critical factor, and so this relatively simple arrangement was satisfactory. An approximate value of 200 ml/min. can be given for the flow rate. The pressure 'build-up' was approximately 1 torr/minute.

In experiments with some gases, the build up of reactions products caused erratic readings of 4047 absorption. For these compounds the pumping speed was increased by opening the exit

valve further. The wider opening required a larger quantity of gas to maintain the same flow rate, hence this procedure was limited by the rapid pressure drop in the reservoir.

An Atlas MMCT or, in the later measurements, a Barotron MKS vacuum gauge was used to monitor the pressure change. Both units were supplied with a capacitor type sensor. This type of detector has the advantage of having a linear response and a sensitivity independent of the nature of the gas. Each unit had a direct reading scale and a recorder output connected to the X-axis of an X-Y recorder.

The X-Y recorder was supplied with an adjustable input impedance to permit matching with the internal resistance of the potential source. On the X-axis the pressure was recorded and on the Y-axis the output of an RCA 1P28 photomultiplier (See Fig 4). The plot represented the cell transmittance vs. pressure, when the 4047A absorption was being followed. In the emission measurements the emission intensity vs. pressure was recorded directly.

The photomultiplier was operated by a high voltage power supply. A better signal to noise ratio was obtained when the photomultiplier operating voltage was kept much below the maximum. Since the recorder

was less subject to interference, it was preferable to increase its amplification rather than use a higher operating voltage for the photomultiplier.

The 4047A monitoring beam was generated by a Hanovia low pressure resonance lamp. It was enclosed in a compartment, maintained at $29 \pm 0.5^{\circ}\text{C}$. The light was collimated and passed through a Pyrex plate to eliminate the 2537A line and prevent the excitation of the mercury in the cell from this source.

The exciting low pressure resonance lamps with water-cooled electrodes were laboratory built. The cooling water was thermostatically regulated at 20°C .

The cell, the light sources and the photomultiplier were enclosed in a blackened wooden box to minimize the effect of stray light. There were four separate compartments to improve light-proofing, and to allow the same unit to be used for absorption and emission measurements.

The exciting 2537A light, emitted by the water-cooled resonance lamps was passed through a filter solution consisting of a mixture of cobalt and nickel sulphates. The concentration of the cobalt sulphate was higher than that recommended by Kasha (62) to

reduce the transmission through the small window in the 4000A region. The solution was circulated by means of a peristaltic pump, through a jacket surrounding the cell and through a coil immersed in a constant temperature bath. Evaporation losses were low, since the filter solution was completely enclosed. Several months of operation did not result in any change of transmittance of the filter solution.

The cylindrical reaction cell was 300 mm in length and 32 mm in diameter, and made of fused silica (Figure 4), with plane parallel Spectrosil windows. The inlet and outlet tubes for the gas were close to the windows to eliminate "dead" space.

The Spectrosil windows were tightly affixed to 1/4 inch i.d. blackened brass tubes which confined the light path. The emerging beam passed through a small compartment, containing the appropriate optical filters. The 4047A absorption was studied with a 4047A interference filter. The "a" band was isolated with a Corning CR 3385 "cut-off" filter, while the "b" band was studied with a Kodak 18A + 0.5 mm Plexiglas combination filter.

iii. Preliminary measurements.

These measurements were made to check the

operation of the system and to test the validity of criticisms of the method made previously.

Callear and Norrish (30) suggested that a serious shortcoming of this method lies in the difficulty of correcting for the diffusion of metastable atoms. Hg^0 formation takes place chiefly in the first few millimeters of the exciting beam path, close to the wall. They have to diffuse to the center, into the detecting beam to be observed. Since diffusion is pressure dependent, its importance will vary during the run, making the correction difficult. In order to assess the importance of this argument, the following experiments were carried out.

One of the exciting lamps was eliminated, so that the 2537Å light entered the cell from only one side. Firstly, the 4047Å monitoring beam was passed along the length of the reaction vessel close to the wall nearest the exciting lamp and the absorption vs. pressure curve was recorded. Then the operation was repeated with the monitoring beam passing through the cell near to the diagonally opposite wall. The absorption curves were identical. Although Callear and Norrish's argument may apply in certain extreme conditions, in the present study it may be neglected.

In the absorption measurements of the Hg^0 atom concentrations at high intensity of the monitoring beam, some deviation from the Lambert-Beer law might have occurred, owing to the local depletion of the Hg^0 atom concentrations by excitation to the ($^3\text{S}_1$) level.

It was found that the Lambert-Beer law was obeyed up to $\sim 25\%$ absorption of the monitoring 4047Å light intensity.

Experiments were also carried out to determine the effect of pressure broadening on the absorption of resonance radiation by the mercury in the reaction cell. One exciting lamp was removed and a blackened brass tube fitted at right angles close to the cell. It was exactly opposite the exciting lamp, so that the 2537Å light passed through the cell before entering the tube. The other end of the tube was fitted into a small light-tight box, housing a 2537Å interference filter and a 1P28 photomultiplier. A new carefully flamed cell was connected via a liquid N_2 cold trap to the vacuum rack. This arrangement prevented contamination of the cell with mercury. The light, passing through the cell, was recorded with and without mercury present. The mercury absorbed about 91% of the 2537Å light. When nitrogen was flowing through the reaction cell this value increased to 96% at 10 torr of nitrogen.

This result indicated a narrow emission line width for the lamp in comparison to the absorption profile of mercury within the cell. The small increase of the absorption with nitrogen pressure indicated a negligible pressure broadening.

In order to check whether the X-Y recorder had significantly fast response, tests were made in which continuously recorded absorption curves were compared with a set of absorption values obtained at fixed pressures. The flow rate was the same in both cases, but the pressure was kept constant for at least two minutes for the fixed pressure readings. These individual points were the same as those obtained from continuous recording, hence the response time of the X-Y recorder was adequate for the variable pressure runs.

iv. Summary of operating conditions.

The general operating conditions can be summarized in the following way:

<u>4047A light source:</u>	Hanovia resonance lamp; operated at 570V stabilized voltage; temperature $29 \pm 0.5^{\circ}\text{C}$.
<u>2537A light source</u>	operated from a 5000V/60mA current limiting transformer at about 800V; distance from the cell 5 - 10 cm; the absorption of 4047A beam was not more than 23%.

Photomultiplier: Model RCA 1P28; operating voltage for, a. adjusted to give full deflection in 4047A absorption measurement, approximately 475V; b. always 540V in emission measurements.

Pre-amplifier: laboratory built cathode follower, $I_h = 6.3V$, $V_a = 280V$;

X-Y recorder: Hewlett Packard, Model 3001
X-axis: recorded pressure
1 torr/inch or in some cases
3 torr/inch.
Y axis: recorded photomultiplier output; range 50mV/inch;
monitored: a. in absorption measurements the percentage of transmittance. b. in emission measurements, the light intensity directly;

Filters: Band "a" Corning CR 3385 'cut-off' filter; Band "b" Kodak 18A + 0.5mm Plexiglas; Monitoring 4047A beam 4050A interference filter; Filter solution 300g/l NiSO_4 , 120g/l CoSO_4 in water, circulated at 24°C.

Flow rate: approximately 200 ml/min; measured with a rotameter; adjusted with Edwards needle valve;

Pressure gauges: Atlas MMCT capacitor type; or Barotron MKS capacitor type.

3. Measurement of emission from the intermediate complex (Hg-molecule)*.

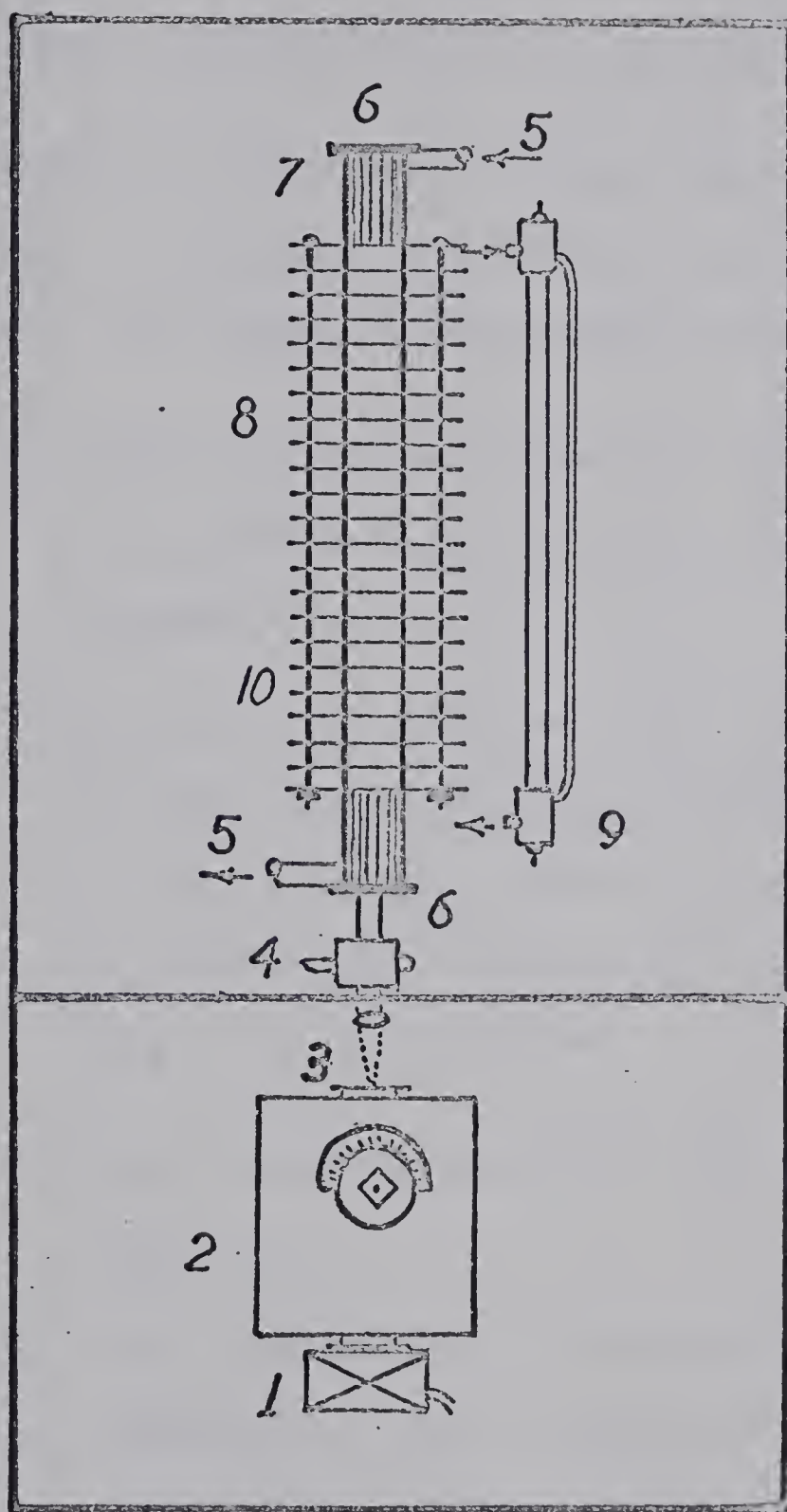
The vacuum system was the same as described in section 2 of this chapter. The reaction cell (Figure 5) was made of Spectrosil to eliminate the emission interference of fused quartz (63). It was a cylindrical tube, 140 mm long and 12 mm in diameter. Both ends were sealed with plane, 1/8" thick LiF windows. The outlet and

inlet tubes were sealed close to the ends to ensure complete circulation of the substrate. The illuminated center section was 120 mm long. Closely spaced, blackened brass plates collimated the exciting beam to reduce light scatter.

The exciting light source was a water-cooled low pressure resonance lamp. A second cell was placed in the fluorescence path, which contained 1 atm. cis-butene (2) and a few drops of mercury. This served to eliminate the 2537Å radiation originating from scatter and from the resonance phosphorescence of the excited mercury in the reaction cell.

The emerging light was focused with a Spectrosil lens on to the entrance slit of a Bausch and Lomb grating monochromator. Owing to the low emission intensity, large slit openings were required which resulted in a low resolution. This low resolution was satisfactory for the limited aims of the present studies.

In a similar, simpler arrangement, a 2800Å interference filter was used in place of the monochromator, which gave a better signal to noise ratio. The recording system was the same as that described in Chapter II 2.



- | | | |
|-------------------------------|-------------------------------------|-----------------------|
| 1. photomultiplier | 2. monochromator | 3. collimating lens |
| 4. 2537A filter
(butene-2) | 5. inlet and outlet | 6. LiF windows |
| 7. blackened ends
of cell. | 8. blackened collim-
ator plates | 9. 2537A light source |
| 10. reaction cell | 11. wooden box | |

Figure 5

Cell unit for the (Hg-molecule)* excited intermediate emission.

CHAPTER III RESULTS

1. Energy transfer involving an excited intermediate

Figure 6 and Table 2 present emission data for a series of compounds using the 2800A interference filter. The results may be summarized as follows:

1. Emission was not observed from Hg mixed with $\text{H}_2, \text{D}_2, \text{NO}, \text{CO}, \text{C}_2\text{H}_4, \text{C}_2\text{F}_4, \text{C}_2\text{HF}_3, \text{C}_2\text{H}_2\text{F}_2, \text{C}_2\text{H}_3\text{F}$ and CH_3CHO .
2. Emission was observed from Hg mixed with $\text{CH}_4, \text{CD}_4, \text{C}_2\text{H}_6, \text{C}_2\text{D}_6, \text{C}_3\text{H}_8, \text{C}_3\text{D}_2\text{H}_5, \text{C}_3\text{D}_6\text{H}_2, \text{n-C}_4\text{H}_{10}, \text{i-C}_4\text{H}_{10}, \text{neo-C}_5\text{H}_{12}, \text{neo-C}_5\text{D}_{12}, \text{N}_2, \text{cyclo-C}_3\text{H}_6, \text{cyclo-C}_3\text{D}_6, \text{H}_2\text{O}, \text{D}_2\text{O}, \text{NH}_3, \text{ND}_3, \text{CF}_4, \text{Ar}, \text{Kr}, \text{Xe}, \text{Ne}$.
3. Every examined paraffin mixture exhibited emission.
4. The lower emission intensity from nitrogen, compared to that of methane, indicates that there is no obvious correlation between the Hg^0 atom concentrations and the emission intensity. Methane produces no Hg^0 atoms,

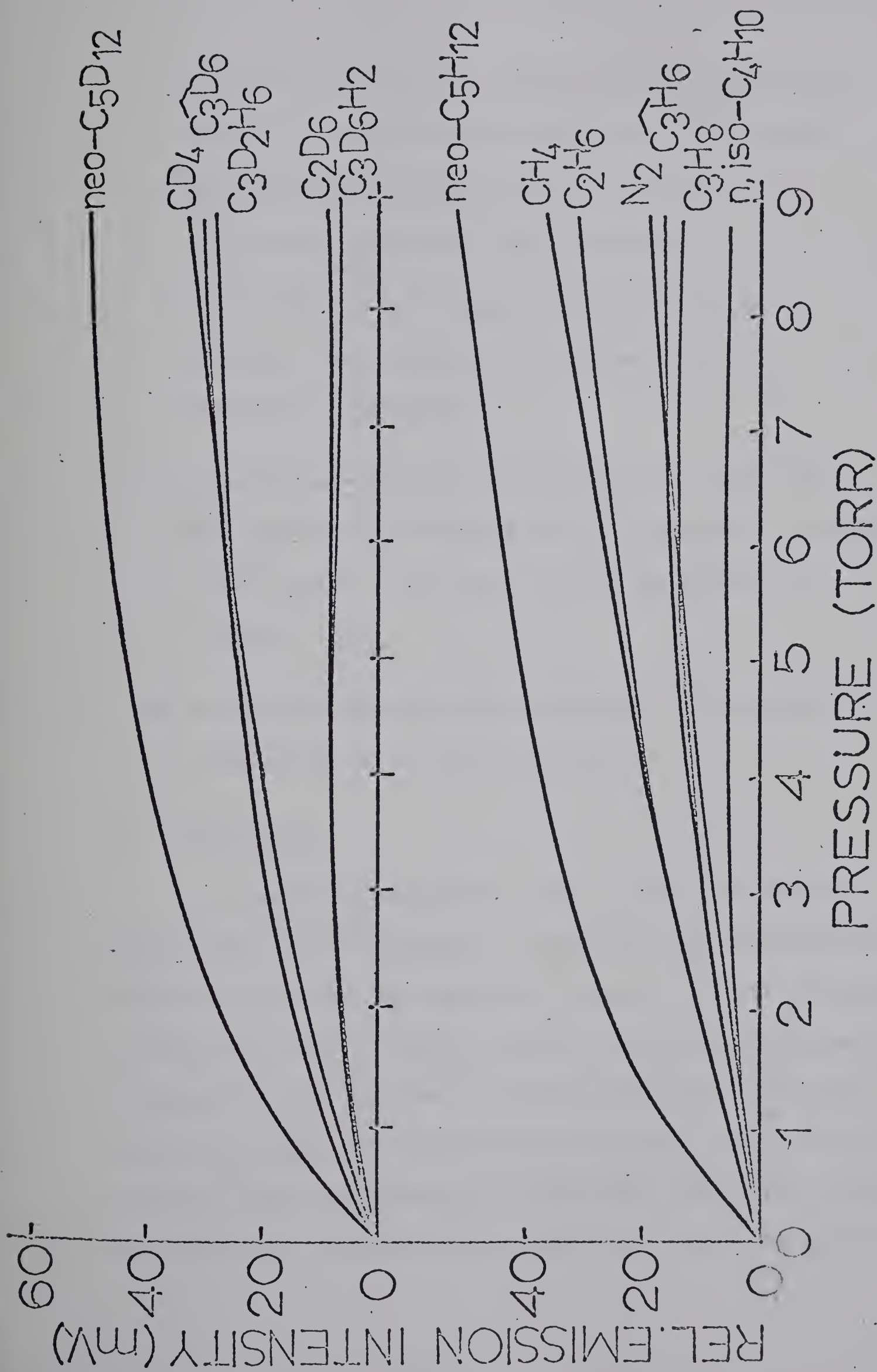


Figure 6

Relative emission intensity vs. energy acceptor pressure

yet its emission is stronger than that of N_2 , which is an effective producer of Hg^0 atoms.

5. The emission shows a linear dependence on the 2537Å exciting light intensity.
6. The addition of a small amount of NO to the emitting mixture did not affect the emission intensity.
7. Ethane and propane pressures up to 500 torr did not quench the emission, suggesting a short, ($<10^{-9}$ sec.) lifetime for the intermediate (Figure 7).
8. Deuterium substitution affected the emission intensity in a complex manner.

ii. Discussion

It has been suggested above, that the emission did not appear to be related to the Hg^0 atom concentration. This observation is supported by the lack of an appreciable effect of adding a small amount of NO on the emission intensity (see section 4 of this Chapter), and the anomalous behaviour of deuterated compounds. It is therefore evident that the emission originates from the excited intermediate formed between Hg^1 atoms and the substrate

TABLE 2

Complementary list of compounds examined for complex intermediate emission.

Substrate	Emission	Substrate	Emission Region (Å)	Rel. Intensity
H ₂ , D ₂	Nil	CF ₄	2540-2600	approx. 1/2 of CH ₄
NO, CO	Nil	H ₂ O, D ₂ O	2540-3200 (max. ~2750)	approx. 100 times that of paraffin emissions
C ₂ H ₄ , C ₂ F ₄	Nil	NH ₃ , ND ₃	2900-4000 (max. ~3600)	approx. 100 times that of paraffin emissions
C ₂ HF ₃ , C ₂ H ₂ F ₂	Nil	Ar, Kr, Xe	2540~3100	approx. 100 times that of paraffin emissions
C ₂ H ₃ F, CH ₃ CHO	Nil			

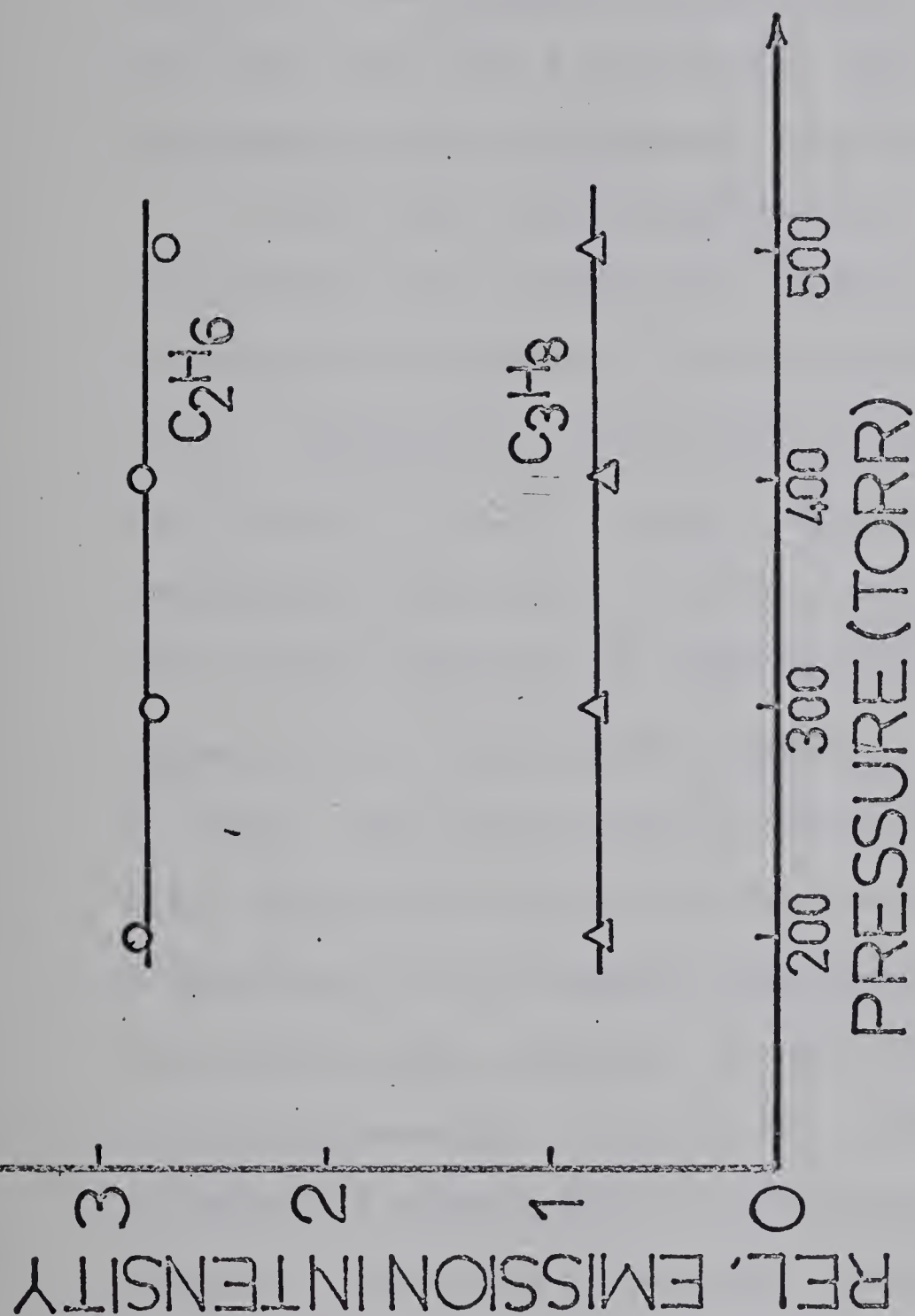


Figure 7. Relative emission intensity vs substrate pressure.

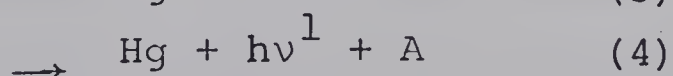
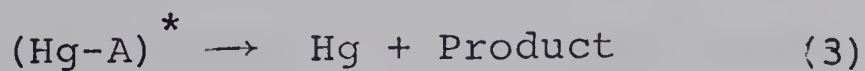
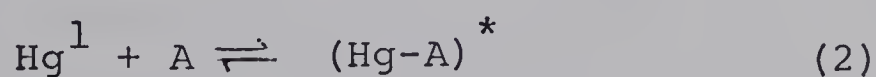
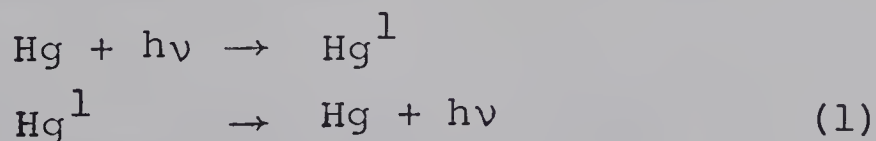
(Note: The readings are corrected for incomplete quenching.)

atoms or molecules. The existence of such intermediates had been suggested by a number of early workers (54,55). The complex emission was observed in only a few cases, CH_4 (57) and Ar,Ne, (56), but it was overlooked during subsequent developments in the field.

It has also been suggested that the intermediate responsible for the emission is held together by weak polarization forces and has well-defined electronic states (56). The species are probably similar in nature to Hg_2 , the diatomic mercury excimer molecule. Hg_2 has several bonding excited electronic states, but the ground state is very weakly bonding and spontaneously decomposes at room temperature. The emission maximum in most cases is close to 2537Å, the wavelength of the exciting radiation but with ammonia the energy difference is some 30 kcal/mole. A fraction of this energy difference can presumably be retained by the substrate in the form of vibrational and rotational energy. Thus we may infer that a partial transfer of energy from an electronic state to an acceptor molecule is possible. In the case of ammonia for example, it would be possible to raise the molecule to the $(3v)$; $(v_1 + 2v_3)$ or $(3v_1 + v_4)$ vibrational states. An extreme case for the decay of the excited complex would be dissociation into ground state mercury atoms, and a vibrationally excited acceptor molecule without

emission. An example of this process is the $(\text{CO-Hg})^*$ complex. This intermediate is exceptionally long-lived and readily undergoes bimolecular energy transfer reactions (58). Alternatively, it may decompose into CO^* and Hg giving no spontaneous emission. The CO^* molecules up to $V=12$ have been detected (21) by IR emission spectroscopy. The maximum retained vibrational energy corresponds to about 60 kcal/mole, while the missing $112-60 = 52$ kcal/mole, presumably appeared in the translational energy of the fragments.

As illustrated by the example of carbon monoxide, the energy transfer may well occur via a transient complex even in those cases where no direct spectral evidence has been found to indicate their presence. A reversible complex formation, as a general mechanism for energy transfer, has been postulated by Schenck (64), which, in the case of Hg^1 atom can be written in the following way:



The emission intensities with and without the quenching gas A, R and R^0 respectively can be expressed under steady illumination as

$$R^0 = k_1 [Hg^1] \quad (III-1)$$

$$R = R^0 - k_4 (Hg-A)^* \quad (III-2)$$

It is assumed that the intensity arising from reaction (5) has negligible importance compared to reaction (1). The quenching is defined as the emission ratio

$$\frac{R^0}{R} = \frac{k_1 [Hg^1]}{k_1 [Hg^1] - k_4 (Hg-A)^*} \quad (III-3)$$

Using the steady state approximation to calculate $(Hg-A)^*$ concentration, the expression becomes

$$\frac{R^0}{R} = \frac{1}{1 - \frac{k_2}{k_1} \frac{k_4 (A)}{k_3 + k_4 + k_5}} \quad (III-4)$$

Neglecting the higher members of the series we obtain

$$\frac{R^0}{R} = 1 + \frac{k_2}{k_1} \left(\frac{k_4}{k_3 + k_4 + k_5} \right) (A) \quad (III-5)$$

Since $1/k_1$ is the lifetime of Hg^1 atoms τ , and $1/(k_3 + k_4 + k_5)$ is the lifetime of the complex, τ_i , the above expression can be written

$$\frac{R^O}{R} = 1 + k_2 \tau \tau_i k_4 (A) \quad (\text{III-6})$$

This expression can be compared to the Stern-Vollmer (4) formula

$$\frac{R^O}{R} = 1 + k_S \tau (A) \quad (\text{III-7})$$

where k_S is the rate constant for the reaction



It is therefore apparent that the quenching cross section, when the intermediate formation is considered, differs from k_S to the extent that the expression also contains the rate of formation, decomposition and lifetime of the intermediate complex. It is not possible to separate the individual factors since they vary independently of one another. It is however, easy to see that the relative importance of the various decomposition routes of the intermediate depends on the molecular structure, which determines, the extent of decomposition, the amount of emission and Hg^0 formed. The observation of the emissions of CH_4 and CF_4 systems can be cited as an example. The intermediate formation in CF_4 is about 1/10 of that observed in CH_4 because of the difference in quenching rates. This would be the expected emission intensity rate, but in fact a ratio of $\frac{1}{2}$ was observed. This is explained by the fact that the rate of reaction 4 is less important in CF_4 , so that a higher percentage of the excited

complex decomposes via emission. This observation supports the conclusion that the relative importance of the various modes of decomposition cannot be predicted from the quenching cross section value of the substrate.

The energy transfer mechanism, as a crude first approximation, can be discussed in terms of an interaction between the excited merucry atoms and paraffin molecules regarded as being a diatomic species. This assumption may be made, since it has been shown that the acceptor molecule undergoes fragmentation at the bond to which the energy is transferred (e.g. no C-C split occurs) (19). A schematic representation of the detailed steps of energy transfer is represented in Figure 8.

The Hg^1 and RH can be envisaged as approaching each other, on a slightly attractive potential surface with a shallow well, corresponding to a loose intermediate complex. Stabilization of this complex requires some degree of energy redistribution within the molecule. The efficiency and speed of this intramolecular energy redistribution and the depth of the potential well will govern the efficiency of the process, which in turn may have a decisive effect on

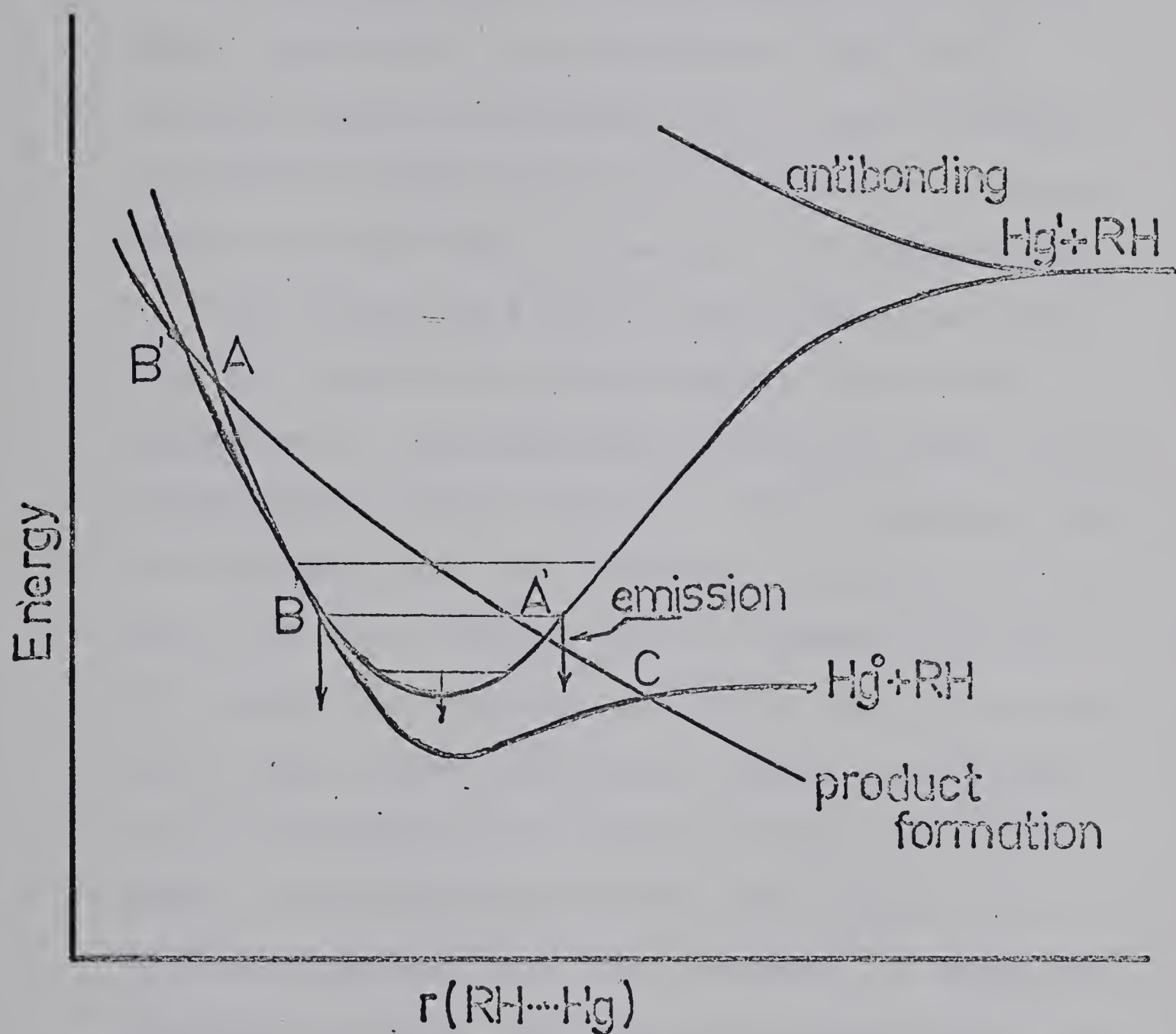


Figure 8. A schematic representation of $\text{Hg}^1 + \text{RH}$ potential energy curves.

the rate constant of the energy transfer. It should be emphasized that a diatomic model of the reaction does not take into consideration the number of oscillators in the molecules, or their force constants. The existence of this loose complex would be consistent with a small negative activation energy for the energy transfer reaction which has been found to the case for propane (59).

At the points A and A^1 the complex can cross over to a potential surface which leads to the formation of a ground state mercury atom and to the fragmentation of the acceptor. It is apparent that the crossover at A will dominate so long as it is below 112 kcal. However when A is above 112 kcal i.e. above the energy of Hg^1 atoms, the cross-over at A^1 would become important. Since the position of A is related to the energy of the bond to be broken, deuterium substitution will result in a different position for the intersect. A change in the position of A, particularly if the position is above 112 kcal, will markedly affect the product yield. Therefore one would predict a lower decomposition yield in those cases where the interaction involves the C-D bond (cf. $CH_3CH_2CH_3$, $CH_3CD_2CH_3$ and $CD_3CH_2CD_3$).

The efficiency of the cross-over at A will

determine the fraction of the intermediate complex trapped in the potential well. These intermediates will have four alternative modes of decay.

- (i) cross-over at A^1 to yield products
- (ii) cross-over at B to yield Hg^0 atoms and excited RH
- (iii) decomposition via emission
- (iv) reversion to reactants.

Since the cross-over at A^1 leads to the same product as the cross-over at A, it is kinetically indistinguishable, although its contribution is presumably small. The cross-over at B leads to the formation of Hg^0 atoms. If A is shifted to the higher energies, the relative importance of the cross-over at B will increase, thus the result will be an increased rate of Hg^0 formation. This is in agreement with the observation that on deuteration of the substrate, the concentration of Hg^0 atoms is increased. (e.g. C_3H_8 compared to $C_3D_2H_6$). However the deuterium substitution may have an additional effect on Hg^0 formation. If the cross-over at B is below the $v=0$ vibrational level, the complex will decompose by (iii) rather than by (ii). The decomposition will obey the same rules if B appears at low vibration numbers where the transition will have low probability. When C-H is replaced by C-D, the zero vibrational level is energetically lower, thus the cross-over appears at higher

vibrational levels. Since the result will be an increased probability of cross-over, the Hg^0 atoms concentration should also show an increase. This is in agreement with observation (see examples below).

The decomposition of the intermediate via emission is the third alternative route for the decay. Observation indicates that the head of the emission band is close to the exciting line, thus emission also takes place from higher vibrational levels. There is no data available for the emission quantum yield, but it is very low.

The potential energy surface diagram can provide a qualitative explanation for the low reactivity of Hg^0 atoms. Whether or not the $\text{Hg}^0 + \text{RH}$ energy passes through a minimum with decreasing internuclear distance is not known. Emission from this level could not be detected, possibly because of the overlap with the emission band which originates from $\text{Hg}^1 + \text{RH}$ intermediate complex. There are suggestions in the literature to support both views (21, 58), but it appears to have no bearing on the reactivity of Hg^0 atoms.

The cross-over to the surface which leads to

dissociation occurs at B^1 . When point A appears at higher energy values the cross-over efficiency at B^1 is decreased. This correlates with the observation that the rate of reaction of Hg^0 with deuterated compounds is lower (cf. Figure 43). Summarizing, the steady state concentration of Hg^0 atoms upon deuteration will be higher for two reasons;

- (a) increase of cross-over efficiency at B
- (b) decreased cross-over efficiency at B^1 .

(see Section 2 of this Chapter.)

A limited investigation was carried out on the effect of temperature, from which some qualitative predictions were made.

The decrease of quenching cross section values is noticeable from the data of Yang (59). This corresponds to a decreased rate of stabilization of the collision complex leading to quenching. The increased temperature will hinder the relaxation process by decreasing the cross-over efficiency and thus reduces Hg^0 concentration. Preliminary indications are that in N_2 , where B^1 appears at a very high energy, a relatively modest temperature increase from $20^\circ C$ to $70^\circ C$ decreased the steady state concentration of Hg^0 atoms to about $1/5$. It can be predicted, in hydrocarbons that the cross-over efficiency at B^1 would increase with temperature and as a consequence the emission intensity

would show a decrease. No such studies have been reported in the literature.

A number of compounds can be cited as examples for emission (i.e. propanes, N_2 , CH_4 etc.) but perhaps the comparison of neopentane with ethane is the most interesting;

- (a) neopentane gives a high emission intensity and produces Hg^0 atoms
- (b) ethane gives a relatively high emission intensity, but no Hg^0 atoms.

The interaction of ethane and neopentane with Hg^1 atoms occurs through a $\sigma C-H$ bond. On this basis alone neopentane would be expected to be twice as efficient as ethane in quenching. In fact neopentane is at least 10 times as efficient and this must be the result of a larger number of internal degrees of freedom. This further supports the previous suggestion (page 75), that there must be some coupling between the different bonds. The stabilized complex either emits or forms Hg^0 atoms. Both of these processes are detectable in neopentane, but ethane does not form Hg^0 atoms in detectable concentration. This indicates that the cross-over to the Hg^0 surface appears at lower vibration numbers causing this process to be inefficient. On the other hand the neopentane shows a substantial efficiency for this

cross-over process. This may be interpreted in two ways, either the cross-over appears at higher vibrational levels, or, if it is at the same point, the higher rotational density of neopentane increases the cross-over efficiency.

2. The process $\text{Hg}^1 \xrightarrow{\text{A}} \text{Hg}$

The decay of Hg^1 atoms was monitored by measuring the decrease of the resonance phosphorescence intensity. The measuring unit and the calibration procedures were described in Chapter II./1. Q, the quenching function was obtained from Equation II-4. Values of the product τk_Q were obtained from a plot of $(1/Q - 1)$ vs pressure. A straight line was drawn through the origin using the least mean squares method. The slope represented the quenching relationship $(\tau k_Q/p)$, which is related to the overall physical quenching cross section by

$$\sigma_Q^2 = 2.79 \times 10^{-4} \mu^{-1/2} (\tau k_Q/p) \quad \text{III-8}$$

where the co-efficient was computed for 20°C.

Using values of $k_Q \tau/p$ obtained from the respective plots for each molecule, (Figures 9 to 16) σ_Q^2 can be calculated from Equation III-8. Table 3 lists $(1/Q-1)/p$ and the calculated quenching cross section values. (Note, the lines on Figures are displaced for clarity.)

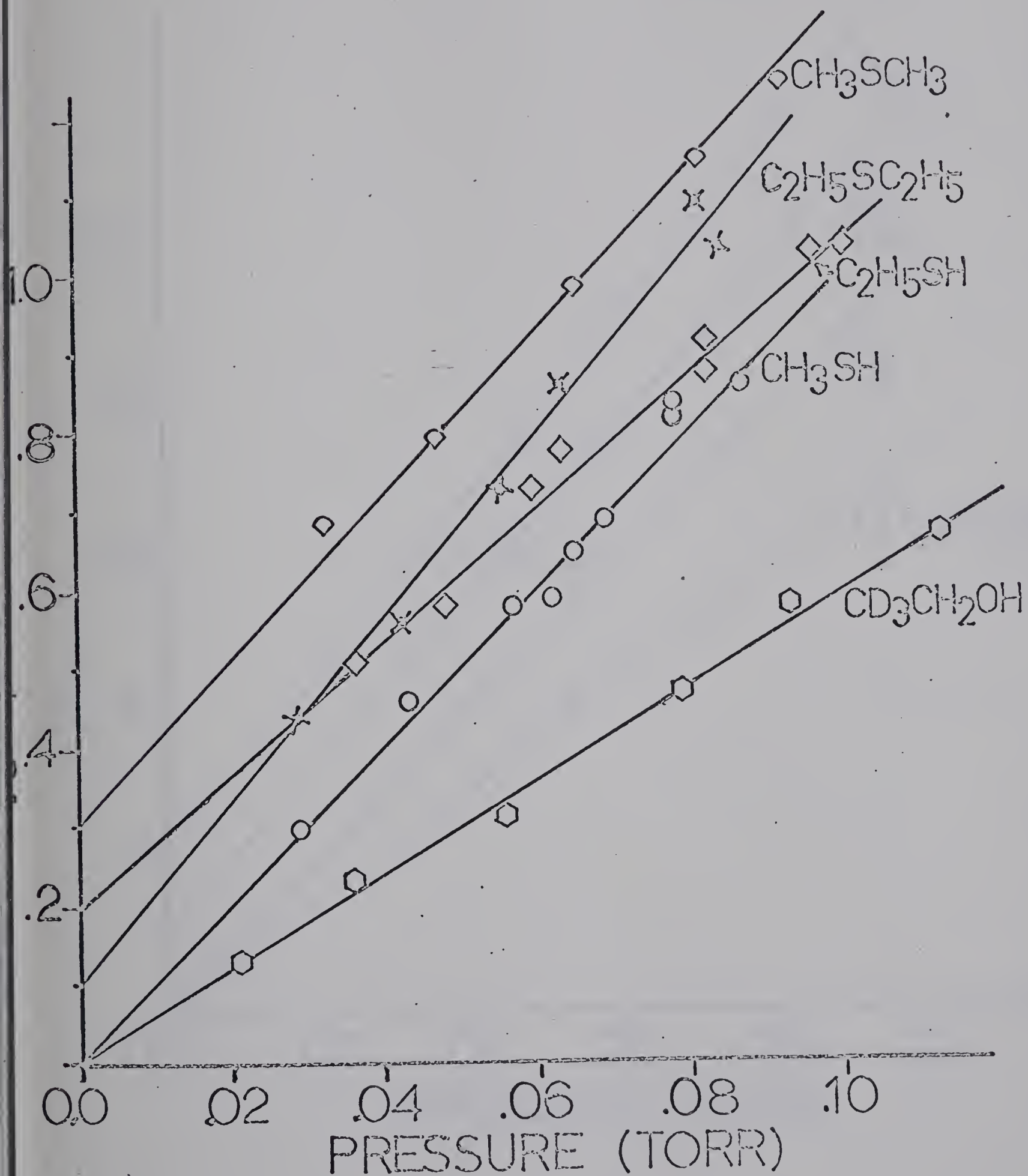


Figure 9. Quenching plots for Hg^1 atoms.

NOTE: Figures 9-16 - each line should pass through the origin, but in some cases have been displaced to accommodate data.

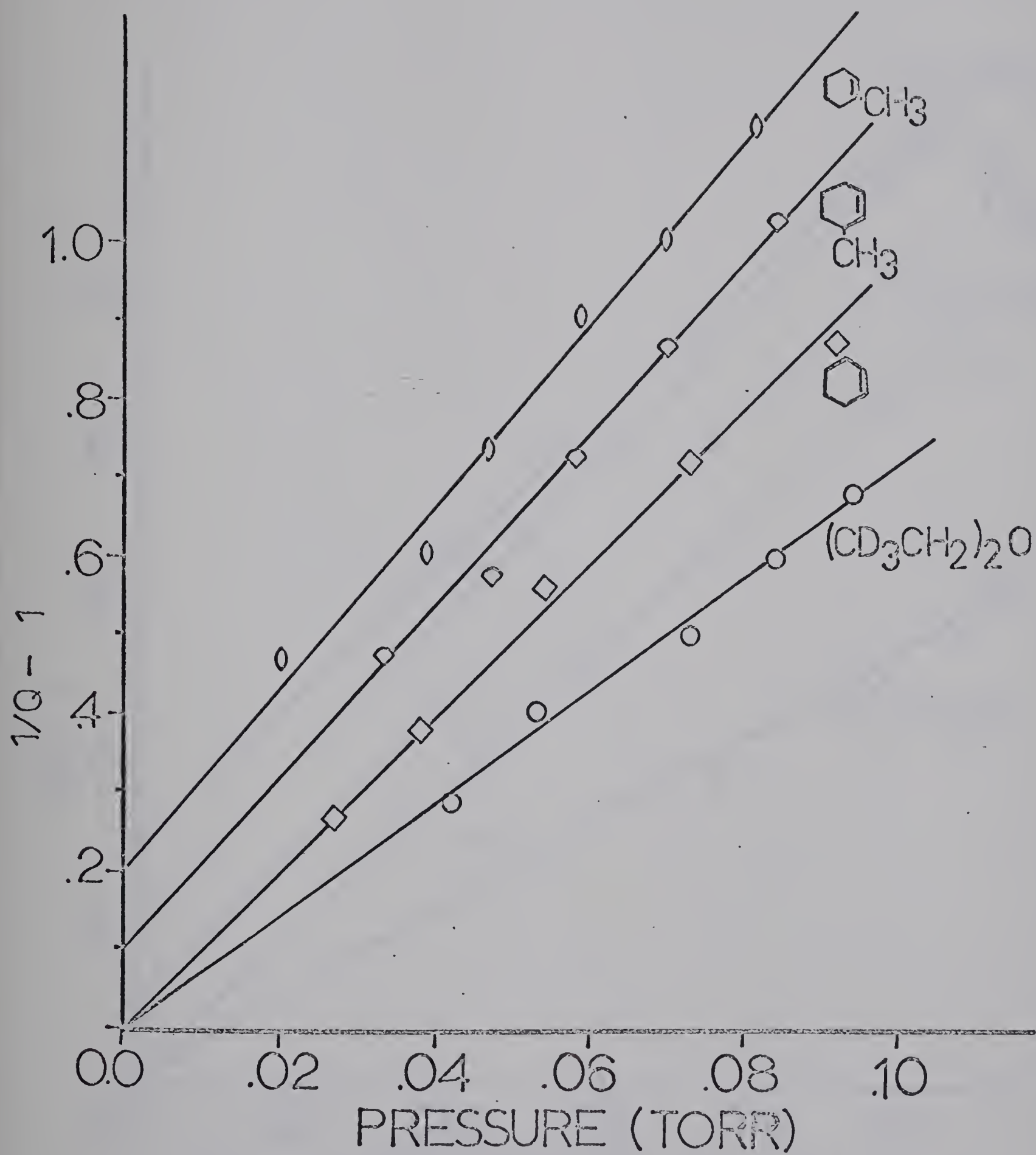


Figure 10. Quenching plots for Hg^1 atoms.

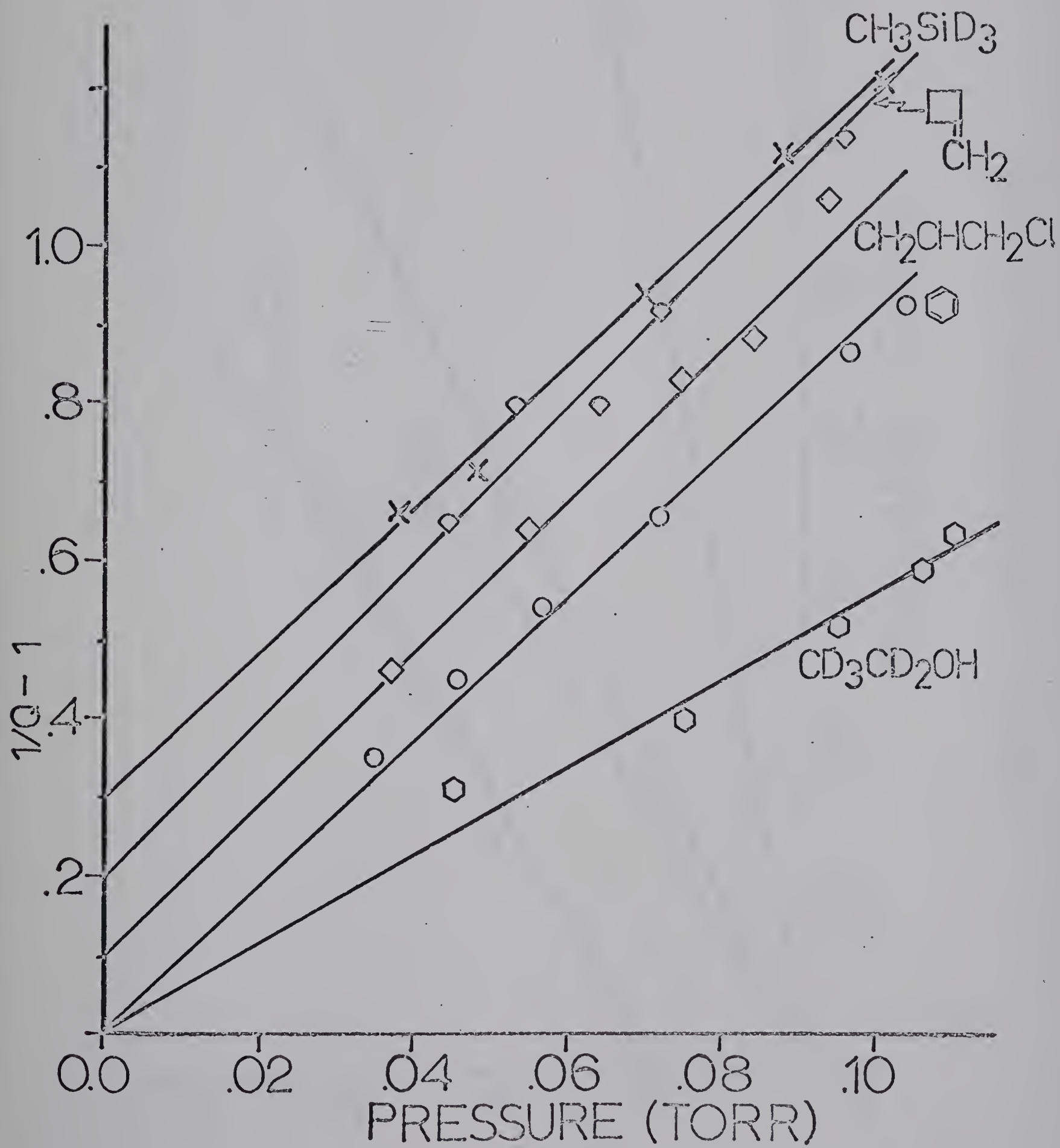


Figure 11. Quenching plots for Hg^1 atoms.

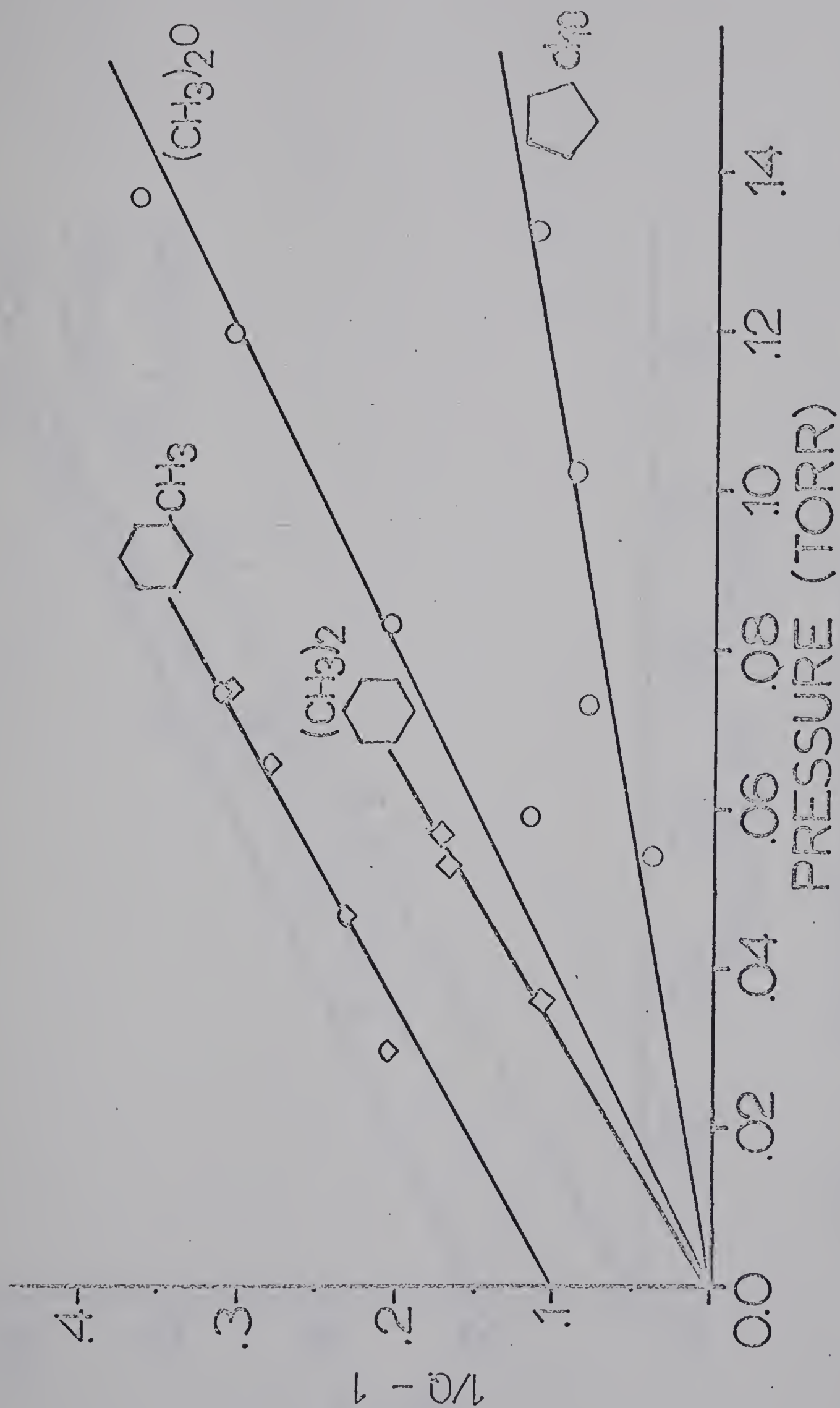


Figure 12. Quenching plots for Hg^{I} atoms.

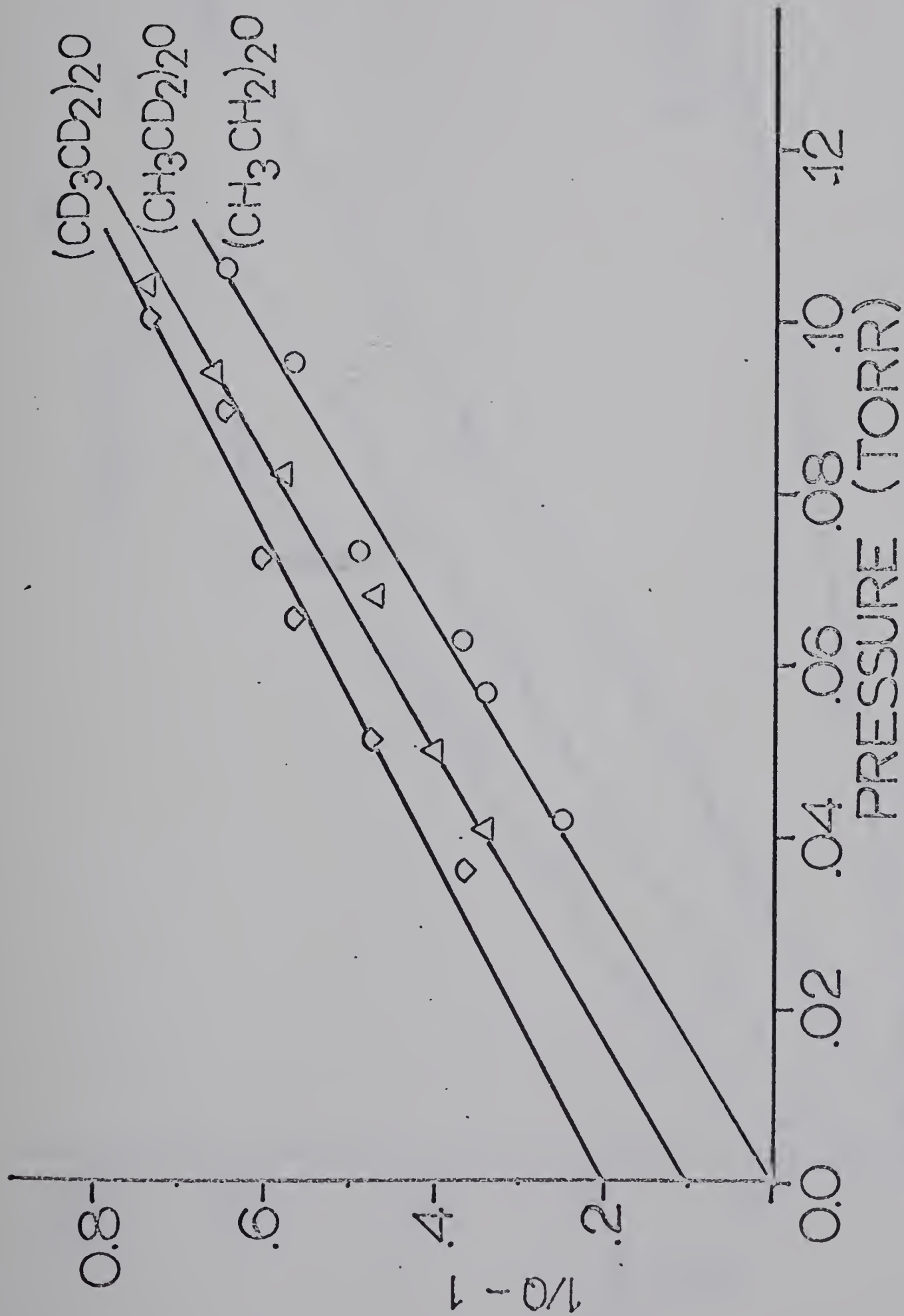


Figure 13 Quenching plots for Hg^1 atoms.

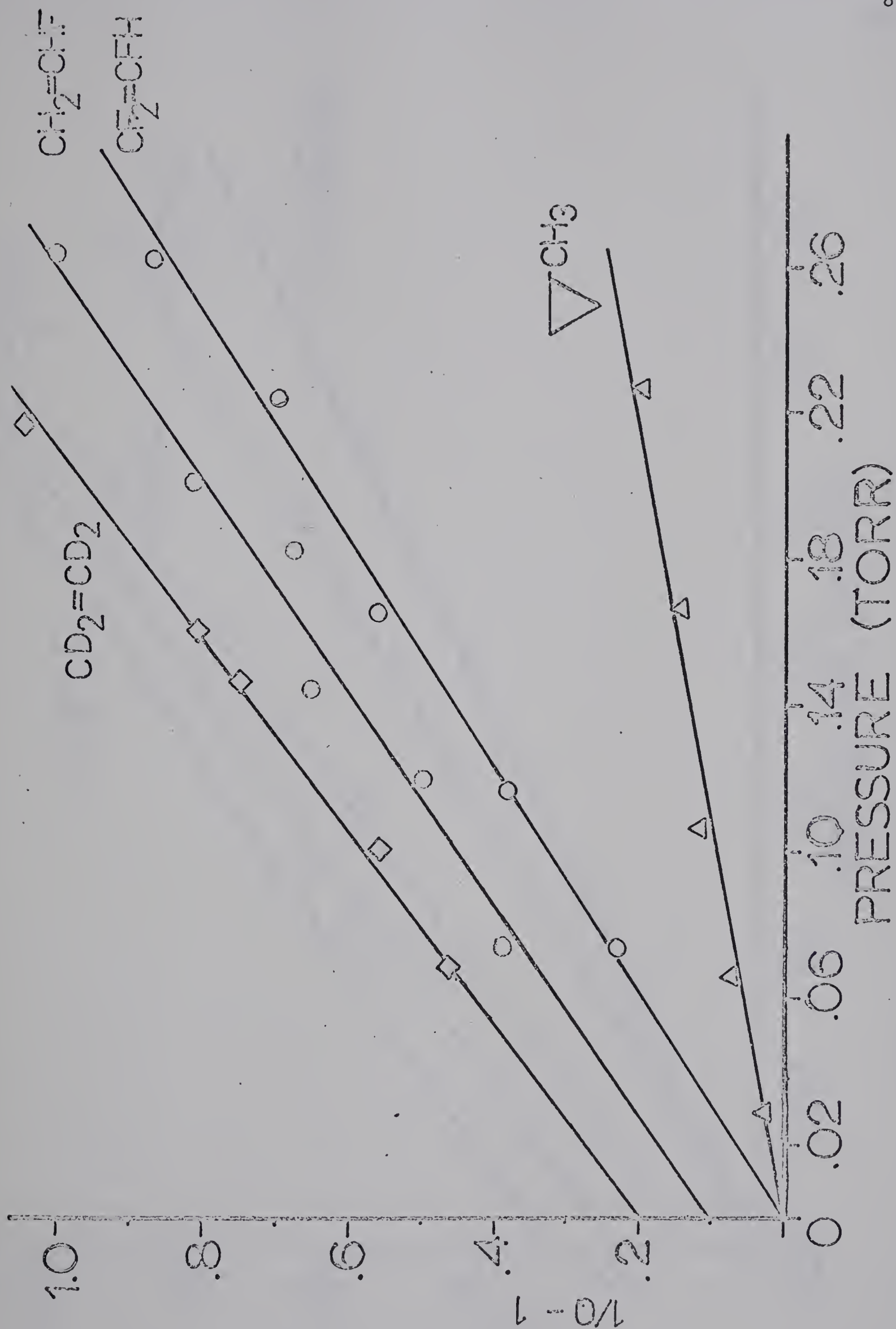


Figure 14. Quenching plots for Hg^1 atoms.

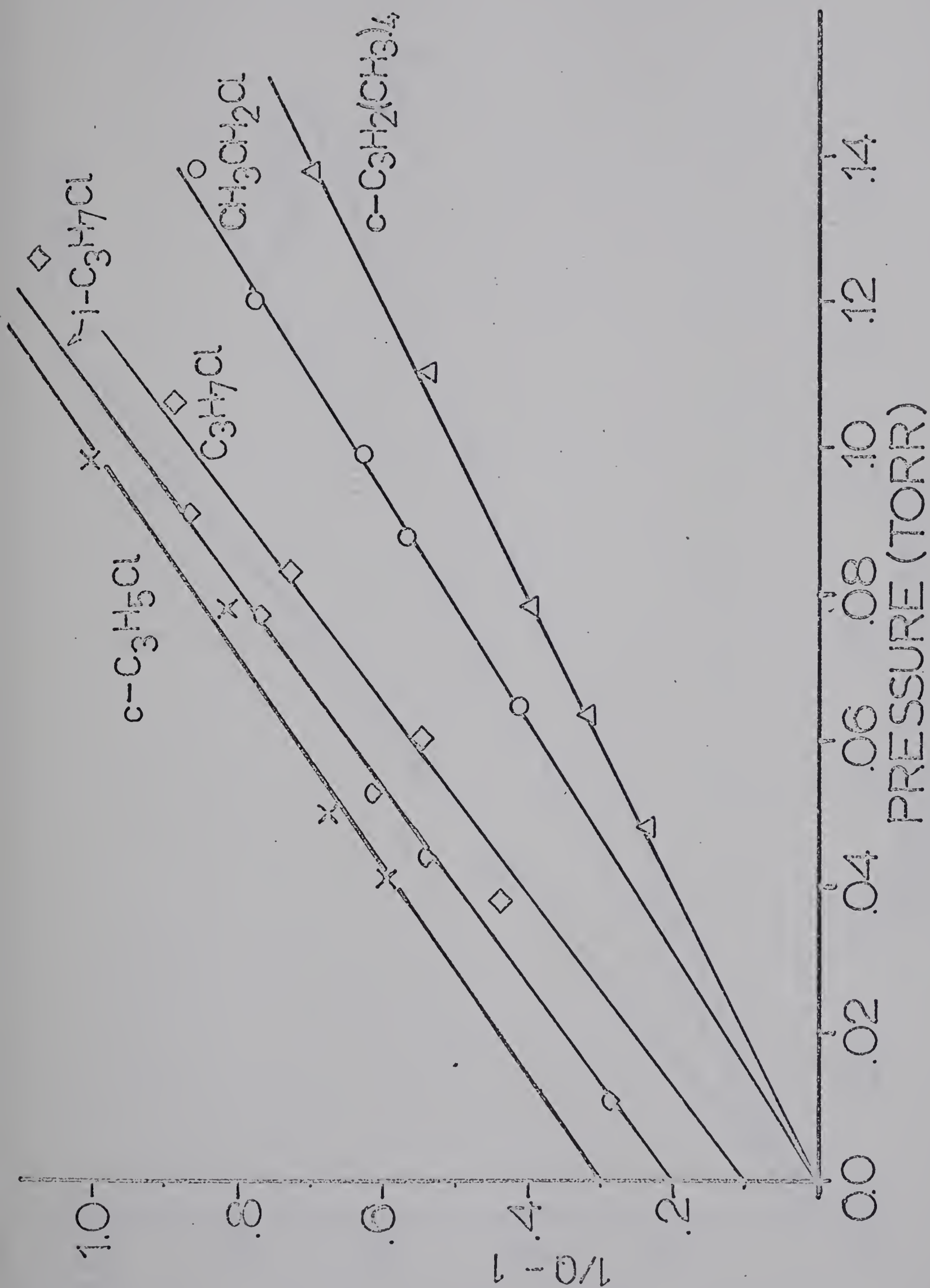


Figure 15. Quenching plots for Hg^1 atoms.

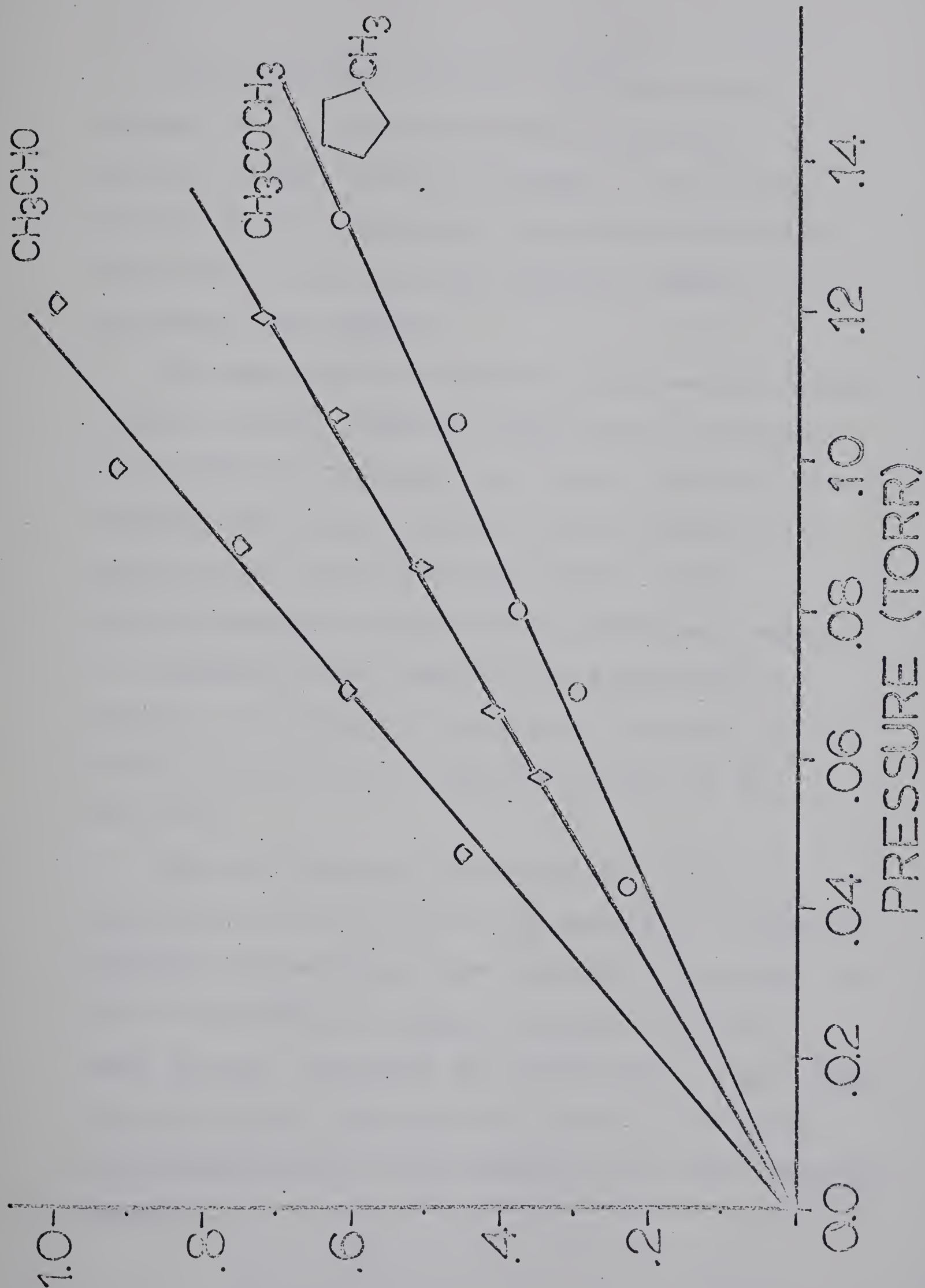


Figure 16. Quenching plots for Hg^1 atoms.

The quenching of benzene, cyclohexane and methanol was repeatedly measured during the period of investigation (5 months). The reproducibility of the measurements demonstrated that the experimental conditions had remained constant throughout this period.

The comparison of quenching cross section values, listed in Table 3 shows that the effect of substitution cannot be described by a simple general relationship. The change cannot be related only to the nature of the substituents but rather to the overall character change of the substituted compound.

Since Hg^1 atoms behave as an electrophilic species, the change of nucleophilic character on substitution must be an important factor in Hg^1 quenching.

Darwent's earlier observation(65), that the substitution of CH_3 , CH_2 and CH results in a specific increment of quenching cross sections in paraffins is due to the different electron donating power of these groups. Similarly the relationship of quenching cross section to the basicity (19), or to the group electronegativity, is also related to the same molecular parameter.

TABLE 3

The quenching of resonance radiation and quenching cross section values.

	$\frac{I/Q - 1}{P}$	σ_Q^2
cyclopropane	0.32	1.85
methylcyclopropane	0.93	6.75
cis-dimethylcyclopropane	1.50	10.6
trans-,dimethylcyclopropane	2.28	11.9
1,1,2,2 - tetramethyl-cyclopropane	5.03	43.2
cyclopropane-d ₆	0.27	1.73
cyclopropylchloride	7.07	55.4
cyclopentane	2.64	19.0
methyl-cyclopentane	4.64	38.
cyclopentane-d ₁₀	0.89	7.3
cyclohexane	2.74	21.8
cyclohexane-d ₁₂	.94	7.9
methylcyclohexane	5.76	50.2
1,1-dimethyl cyclohexane	-	27.7*
cyclohexene	9.8	83.
3-methyl cyclohexene	11.4	100.

contd...

* Reading subject to large error

Note: σ_Q^2 values listed in this Table do not agree with those listed in Table 8 since the latter values are taken from previous publications and they are on a different basis.

TABLE 3 contd.....

	$\frac{I/Q - 1}{P}$	σ_Q^2
4-methyl cyclohexene	10.9	95.
methylene cyclobutane	10.0	81.
ethane	0.042	0.21
ethane d ₆	0.036	0.19
propane	0.43	2.86
propane-d ₆	0.36	2.5
propane-d ₂	0.16	0.99
propane-d ₈	0.12	0.82
n-butane-d ₇	0.42	2.85
ethylene-d ₄	7.71	43.
mono-fluoroethylene	7.0	47.
trifluoroethylene	3.25	27.7
methanol	2.35	13.4
ethanol d ₅	5.50	38.
ethanol d ₃	6.0	39.8
ethanol d ₂	5.20	31.1

contd.....

TABLE 3 contd....

	$\frac{I/Q - 1}{P}$	σ_Q^2
dimethyl ether	2.50	17.3
diethyl ether	6.1	48.4
diethyl ether d ₁₀ (sym.)	5.23	36.3
diethyl ether d ₆ (sym.)	7.10	58.8
diethyl ether d ₄ (sym.)	5.9	48.4
acetone	6.03	43.2
acetaldehyde	8.76	57.1
methyl mercaptan	10.0	67.5
ethyl mercaptan	8.4	62.3
methyl sulfide	10.3	67.5
ethyl sulfide	11.7	100.
ethylchloride	7.50	46.7
n-propylchloride	6.38	62.3
i-propylchloride	7.71	60.6
allylchloride	9.53	76.1
silane d ₄	8.67	46.7
methylsilane d ₃	9.2	62.3

The nucleophilic character of the elements increases within the same group of the periodic table with increasing atomic number. For example, the nucleophilic character changes in the order: $I^- > Br^- > Cl^- > F^-$; and $H_2O > H_2S > H_2Se$ or $CH_4 > SiH_4 > GeH_4$, and the reactivity with respect to Hg^1 atoms follows this same order. This is in agreement with the observation, that for example, sulphur compounds always have higher quenching cross sections than the corresponding oxygen analog.

The nucleophilic character of the acceptor molecule may be considered as the major force governing the complex formation. Owing to the finite rate of energy dissipation necessary to stabilize the complex it can decompose instantaneously, yielding an excited mercury atom and a ground state acceptor molecule. If the intermediate is stabilized, the longer intermediate lifetime must lead to a greater probability of energy transfer, and hence a larger quenching cross section value (cf. Eq.III-6). Thus it is apparent that the complex stability is closely related to the magnitude of the acceptor quenching cross section value, which is therefore a measure of the net rate of complex formation. Collisions leading to quenching require that the initially formed energetic intermediate molecules undergo some degree

of relaxation. This relaxation occurs by an increase in translational energy or by equipartition of the energy among internal degrees of freedom. The increase of translational motion is probably more important in light acceptor molecules such as hydrogen, while the second process of the equipartition of energy has an increased probability with molecules possessing higher internal degrees of freedom. This process was suggested to be important where the interaction involves the $^3(\pi, \pi^*)$ transition, and was used to explain the large quenching cross section value (19). However, the energy re-distribution in paraffins, for example, can be envisaged only by assuming that the primary interaction site couples with other degrees of freedom, eg. stretching, bending etc., of other bonds. This supports the proposal, that the acceptor molecule should be considered as a unit for accepting the energy, and as such, the molecule as a whole determines the quenching efficiency of the collision. The previously quoted examples of neopentane and ethane best exemplifies this behaviour. Despite the fact, that the interaction involves C-H σ bonds, the neopentane possess a fifteen times greater quenching cross section than ethane. This large difference leads to the conclusion that the internal degrees of freedom play an important part in the quenching process.

The experimental observation, that the secondary and tertiary hydrogens are more effective than the primary hydrogens, may also be explained by the effect of coupling with internal degrees of freedom. This effect was observed in propane, which will serve as an example in this case. Since both secondary and primary hydrogens are bound by σ C-H bonds, the apparent higher efficiency of the secondary hydrogens must be related to the increased tendency to stabilize those complexes involving secondary hydrogens. It can be readily seen that the centrally located secondary C-H bonds have greater probability than the terminal methyl hydrogens, to couple with other internal degrees of freedom. This difference will result in the increased importance of secondary hydrogens in energy transfer. This effect is further magnified by the higher polarizability of the secondary C-H bond and its lower dissociation energy.

The interaction of the excited mercury atom with different donors may be summarized in the following way:

(a) the interaction with paraffins must involve the σ C-H bonds. The data in Table 3 reveals a CH/CD isotope effect, although it is smaller than that observed by the chemical method.

(b) Olefins interact mainly via their π orbitals.

Since this interaction is substantial, olefins usually have large quenching cross section values. The reactivity of the π bond is proportional to its electron density, hence the substitution of an electron withdrawing group decreases the quenching cross section.

(e.g. $\text{CH}_2 = \text{CH}_2$ 24.0 $\text{CF}_2 = 9.0$), while an electron donating group increases (e.g. tetramethyl ethylene 43.0) the quenching cross section. Since the C-H bond is not involved in the quenching of olefins they do not show a kinetic isotope effect (e.g. $\text{CH}_2 = \text{CH}_2$ 24.0 compared to $\text{CD}_2 = \text{CD}_2$ 25.0).

(c) Aromatic compounds behave similarly to olefins, their quenching involves mainly their π electron clouds. They have high quenching cross section values.

Cyclopropane is believed to quench in a manner similar to olefinic compounds.

Sherwood, Kozak, Strausz and Gunning (66) reported that the primary process in cyclopropane photosensitization is a ring opening to form a triplet-trimethylene biradical $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\cdot$. This supports the conclusion derived from the very small isotope effect, that the main quenching site in this compound is not the C-H bond.

(d) The consistently higher quenching cross section

values of sulphur compounds compared to those of oxygen analogues is related to their increased nucleophilic character. The experimental data of deuterated ethanols suggest, that not only the oxygen atom, but also the ethyl group and the O-H bond contribute to the quenching. It is not clear why di-ethyl and di-methyl ethers have the same quenching cross section value, but di-ethylsulfide possesses a larger value than the methyl compound (cf. Table 3).

(e) The carbonyl compounds are quenched chiefly by their π and n electrons, the latter is probably the more important of the two. The $\sim 30\%$ greater quenching cross section for acetylaldehyde than that of acetone is probably related to the C-H bonds in the aldehyde group (cf. Table 3).

(f) Fluorine substitution usually decreases, while chlorine increases, the quenching cross section. In halogens the quenching, promotes the transition $n \rightarrow \sigma^*$, which takes place readily in chlorine but for energetic reasons not in fluorine. Fluorine, due to its larger inductive effect, reduces the reactivity of, for example, π bonds with Hg^{I} atoms to a larger extent than chlorine.

(g) The substitution of deuterium in silane showed no isotope effect. This indicates that the large

quenching cross section value of 47 may be due to the quenching of the silicon atom itself. Yarwood et al (13) arrived at a similar conclusion.

3. The process $\text{Hg}^1 \xrightarrow{\text{A}} \text{Hg}^0$

As the concentration of Hg^0 atoms was expected to be small, emphasis was placed on high detection sensitivity. The exciting lamps were placed close to the cell, and as a result the high concentration of Hg^0 atoms in pure N_2 mixtures absorbed 30% or an even higher fraction of the 4047A light intensity. The flow rate of gases was kept constant, but to resolve the sharp maximum which appears in the absorption intensity vs. pressure relationship, a slower pressure build up, approximately 1/2 torr/minute was used. (cf. Figure 17).

Prior to this study only four compounds were reported to produce Hg^0 atoms (30). As is seen from Table 4, these earlier observations were confirmed and in addition fourteen more compounds were found to form Hg^0 atoms from the thirty-five examined. The main features of the observation listed in Table 4 may be summarized in the following way:

TABLE 4

List of compounds tested for 4047A
absorption during mercury photosensitization

Absorption present	Absorption absent
$(N_2, CO, H_2O, D_2O,)$ ^{1.} $C_2H_5OH, CD_3OH,$ $C_2H_2D_3OH, C_2D_2H_3OH, CH_3OH,$ $C(CH_3)_4, C(CH_3)_3CD_3, NH_3,$ ^{2.} $C(CH_3)_2(CD_3)_2, C_3D_2H_6,$ $C_3H_2D_6, C_3D_2H_6, C_4D_{10}$ $(He, Kr, Ne, Xe, CO_2, CH_4)$ ^{3.}	C_2H_4, C_2D_4 $CHF=CHF, CF_2=CHF,$ $NO, N_2O, H_2, D_2,$ $CH_3Cl, cyclo-C_3H_6, cyclo-C_3D_6,$ $(C_2H_5)_2O, C_2H_5SH, (C_2H_5)_2S,$ light straight chain paraff. to C_5

1. Reported previously to form Hg^0 atoms
2. On the basis of 4850A emission
3. Reading is not certain.

1. With the exception of neo-pentane, light paraffins do not show absorption.
2. Except for methane and cyclopropane, deuteration of paraffins results in the appearance of absorption. The substitution of those hydrogens which show the kinetic isotope effect in Hg^1 quenching are usually more effective in producing greater absorption.
3. The substitution of fluorine in ethylene does not induce metastable atom formation.
4. CH_4 , He, Kr, Ne, Xe, and CO_2 produce very small or no absorption of 4047A light.
5. The metastable atoms were detected in water and in methyl and ethyl alcohols, but not in methyl or ethyl ethers.
6. None of the examined sulphur compounds indicated the formation of Hg^0 atoms.

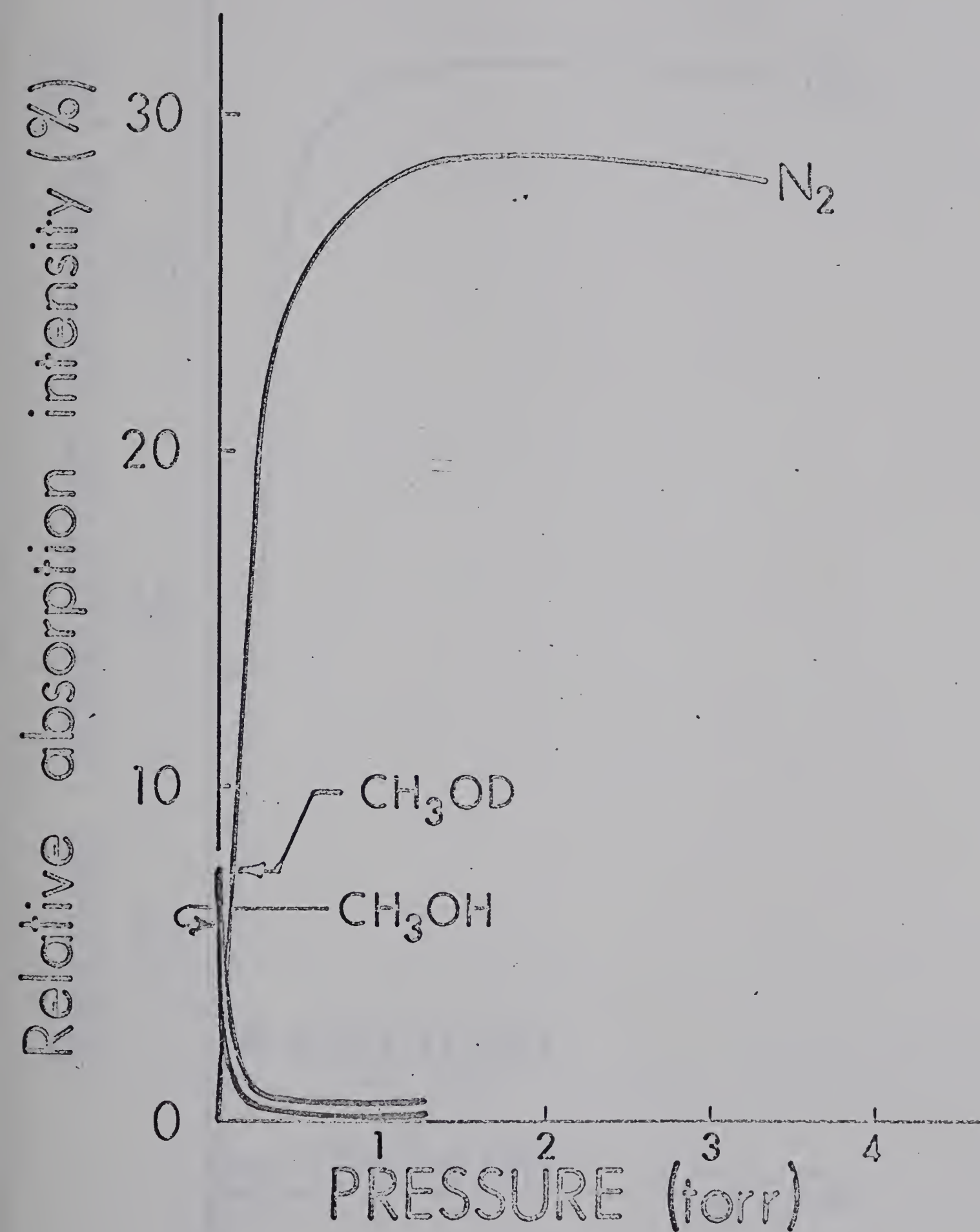


Figure 17

Relative concentrations of Hg^0 atoms in pure ethanol

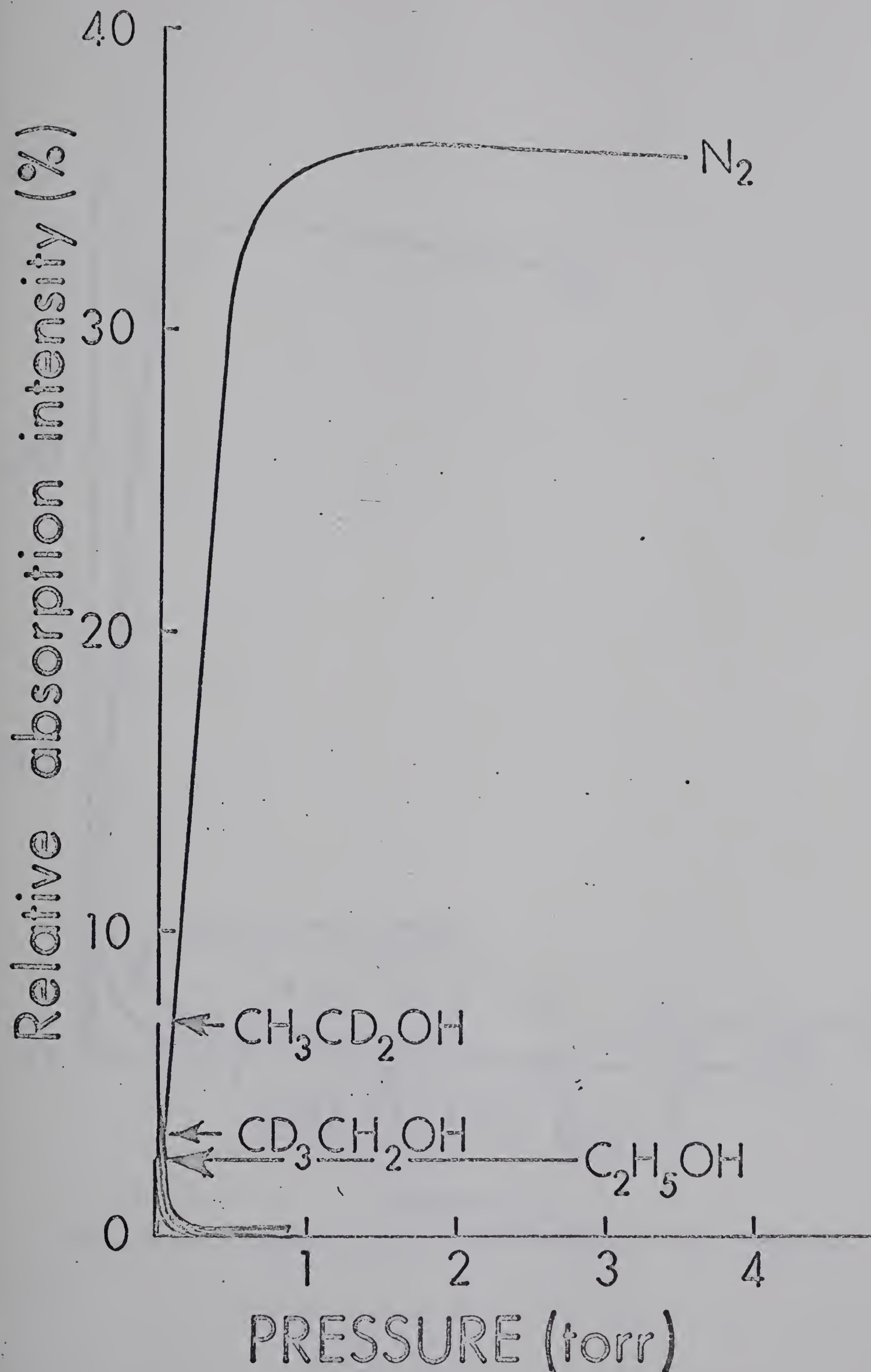


Figure 18
Relative concentrations of Hg^0 atoms in pure ethanol

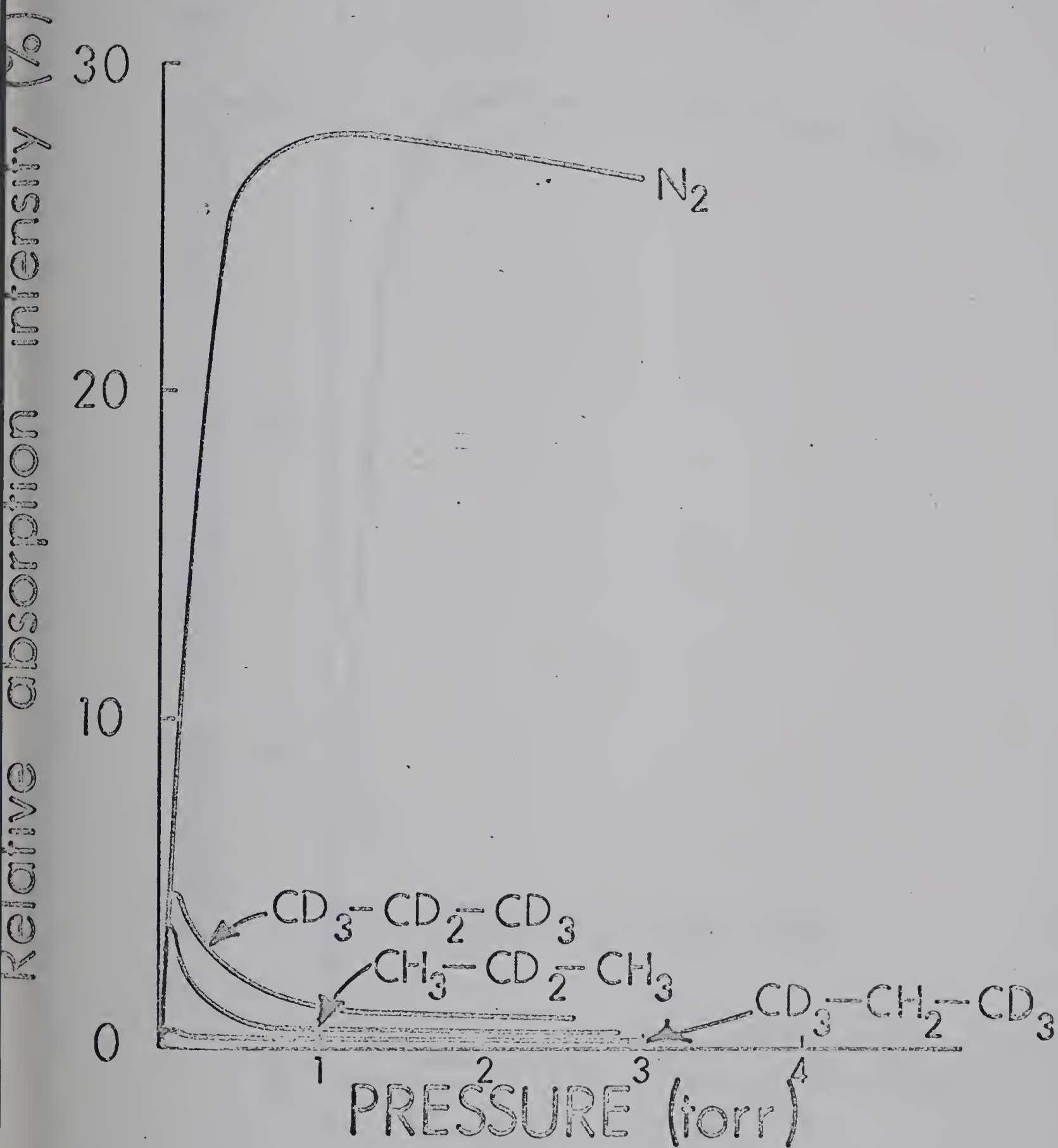


Figure 19
Relative concentrations of Hg^0 atoms in pure propane

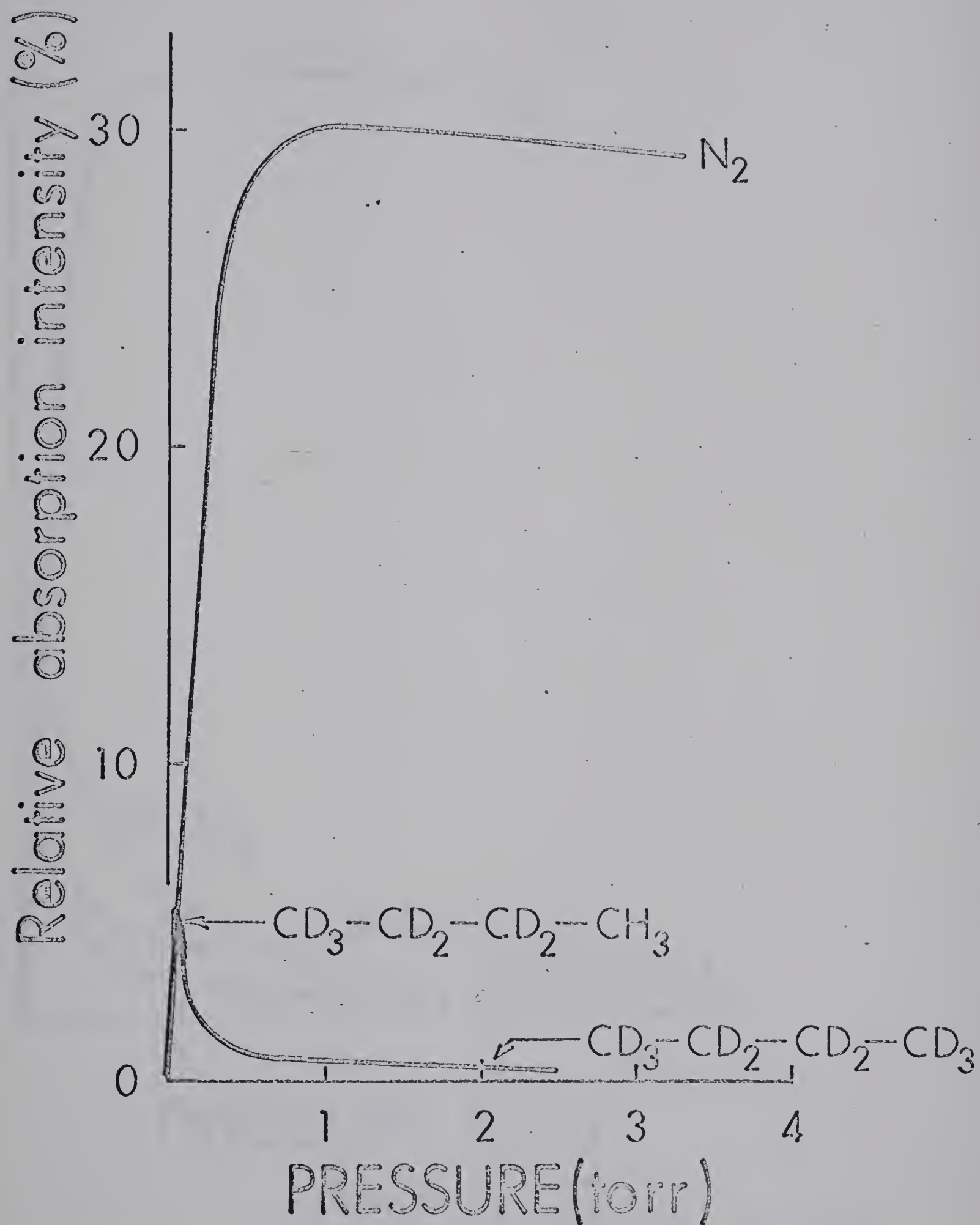


Figure 20
Relative concentrations of Hg^0 atoms in pure n-butane

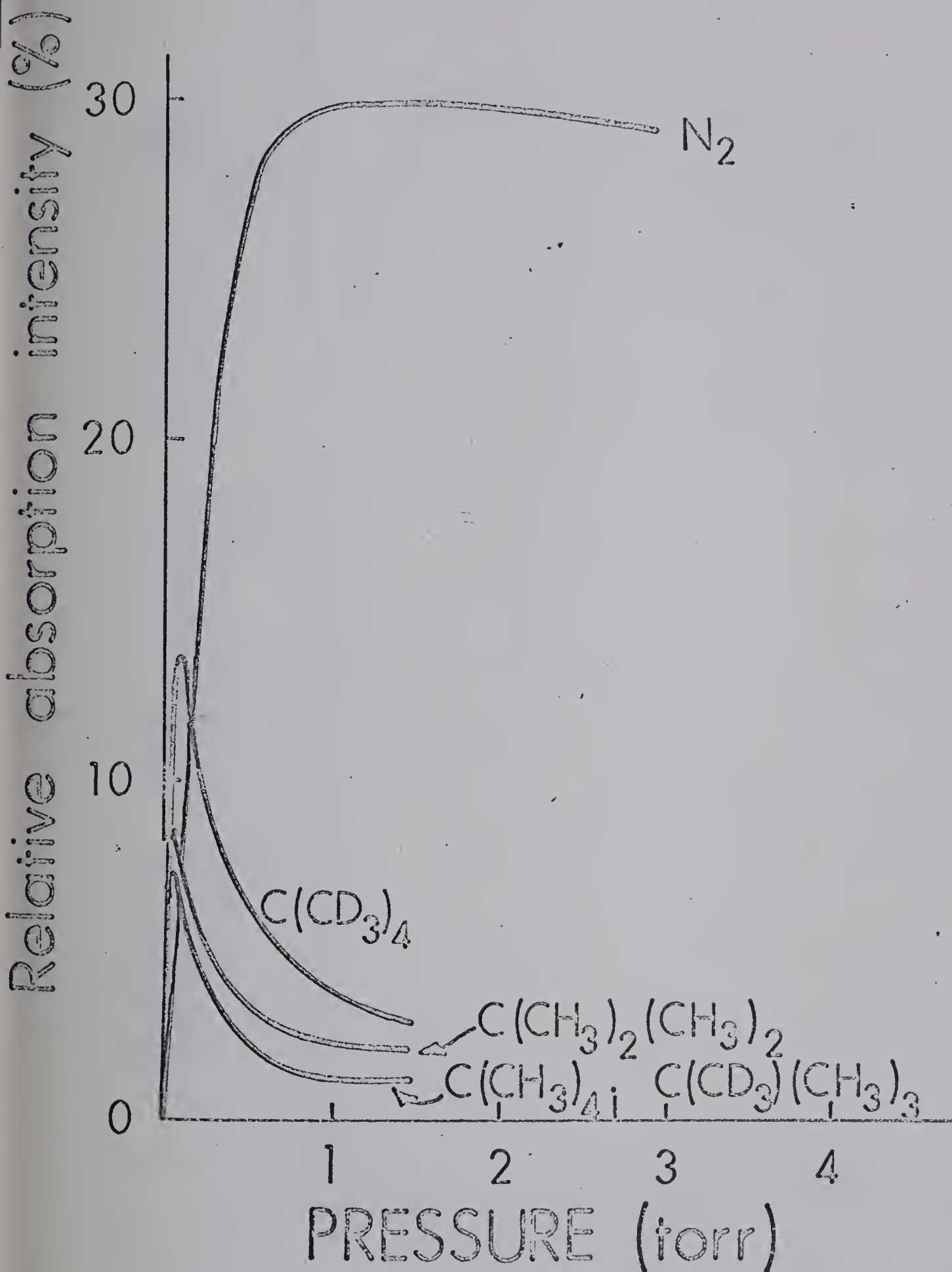


Figure 21

Relative concentrations of Hg^0 atoms in pure neopentane

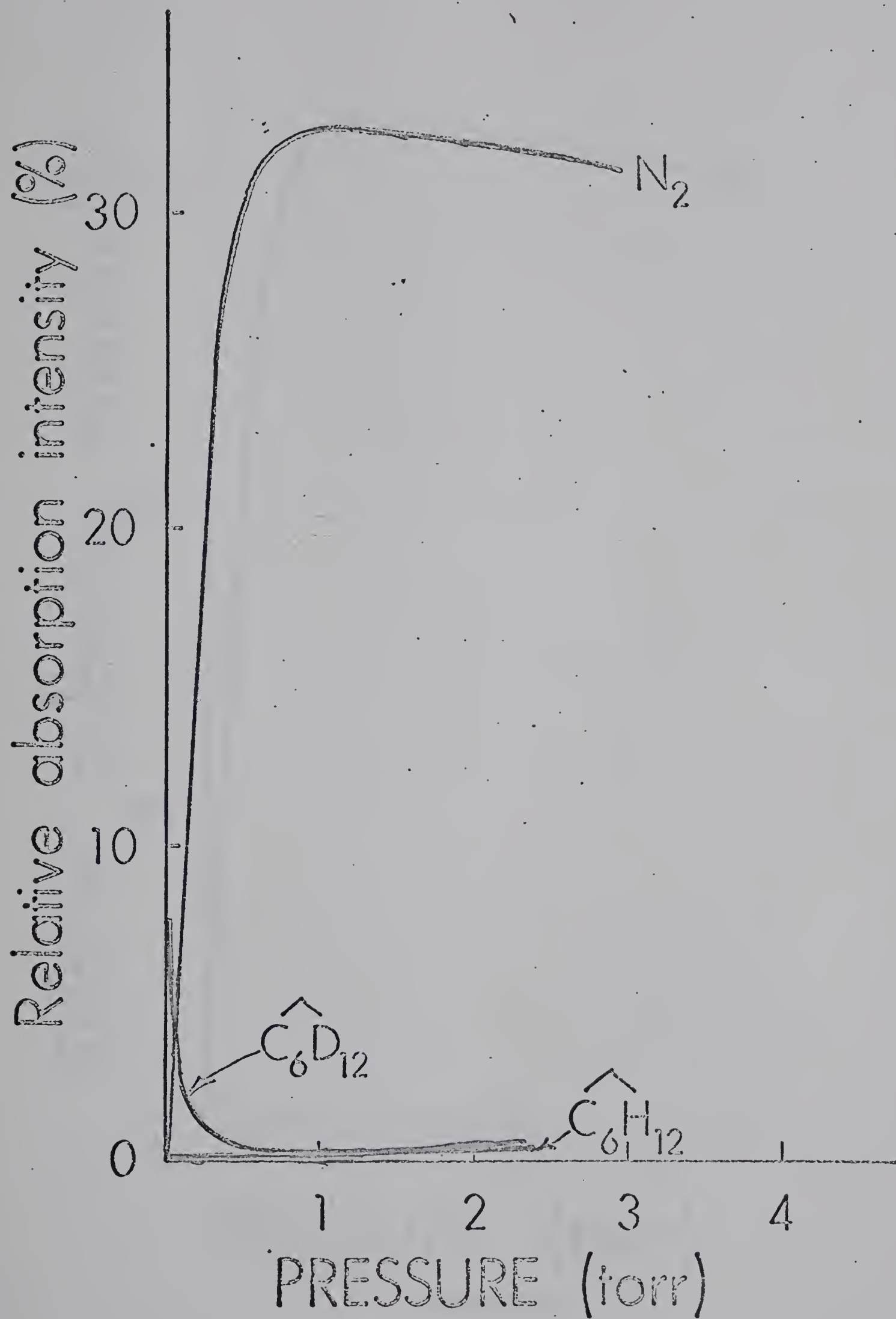


Figure 22
Relative concentrations of Hg^0 atoms in pure
cyclohexane

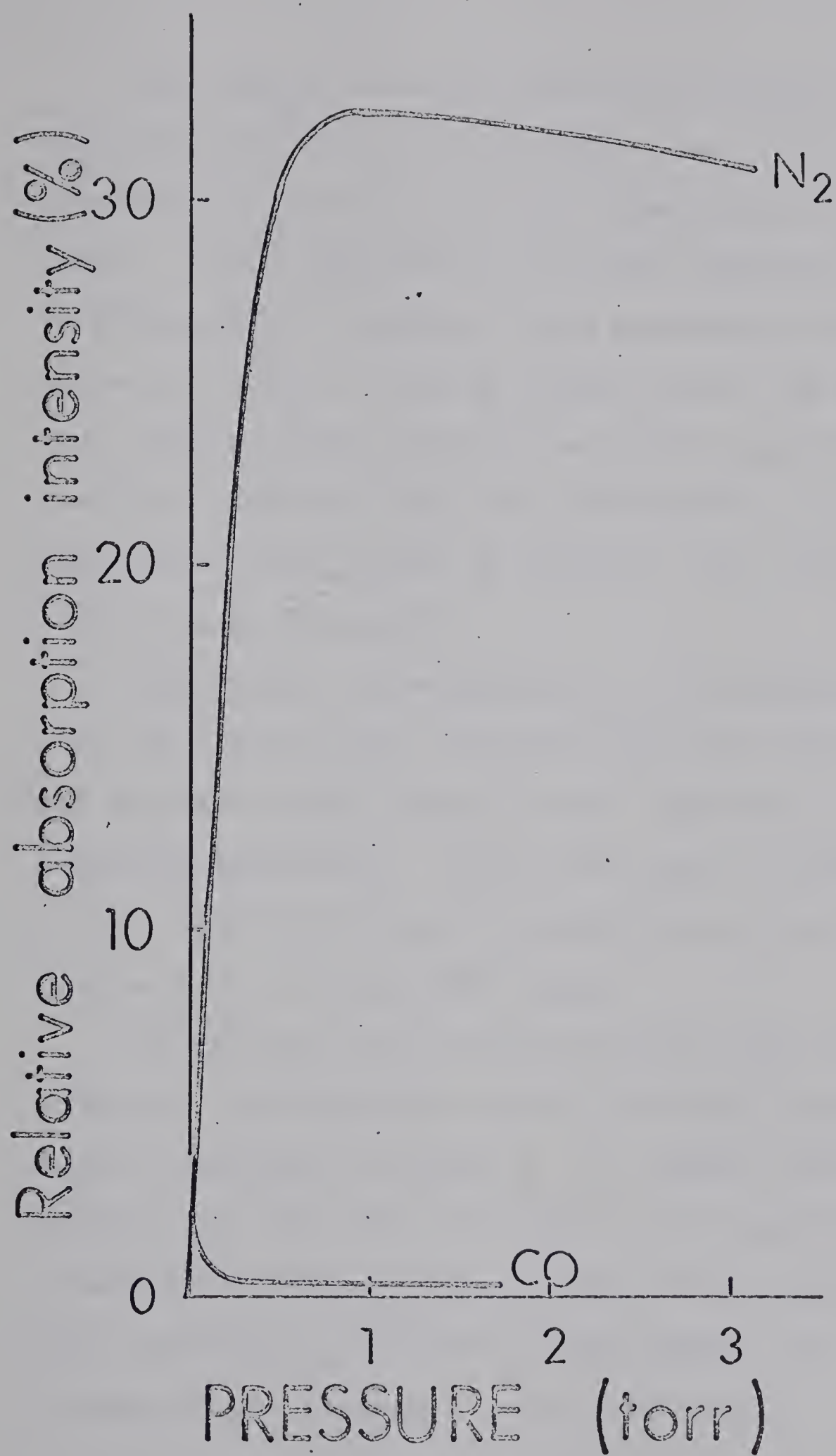


Figure 23

Relative concentrations of Hg^0 atoms in
pure carbonmonoxide

The absence of 4047A absorption indicates a negligible Hg^0 atom concentration, but it does not preclude the possibility of Hg^1 quenching to this level. If the quenching of the Hg^1 resonance level is followed by a further, rapid quenching of the metastable state to the Hg ground state, the Hg^0 atom concentrations will be very small, (eg CO). It is therefore possible that the participation of the metastable state cannot be assessed from the 4047A absorption measurements.

Deuteration was effective in Hg^0 production only when the substitution involved hydrogens which showed the kinetic isotope effect in Hg^1 quenching (e.g. secondary hydrogens). Where the energy transfer did not involve CH bonds, deuteration was also ineffective in forming Hg^0 atoms.

The observation can be explained using the schematic representation of the potential energy curves displayed in Figure 8. It appears from the diagram that Hg^0 atoms can form if the complex intermediate undergoes some kind of stabilization. This relaxation is related to the degrees of freedom of the acceptor. A low efficiency

of the cross-over, which leads to the fragmentation of the acceptor, increases the probability of the complex being trapped in the potential well. Such 'trapped' complexes can either

- (a) decompose via emission,
- (b) decompose to yield $\text{Hg}^0 + \text{RH}^1$.

The relative importance of these alternatives is greater when the cross-over efficiency to the surface leading to product formation is low. If the structure of the acceptor molecule is changed, the importance of the decomposition modes may also change relative to one another. The following example of deuterium substitution in propane will exemplify the above conclusions. The substitution was most effective at the 2,2 position in forming Hg^0 atoms. Non-deuterated propane did not form Hg^0 atoms in detectable concentration, and emission seemed to be the only mode of decomposition for the trapped complex molecules. When secondary hydrogens were replaced, the concentration of Hg^0 atoms became detectable and the emission intensity increased.

Quantum mechanical treatment of the harmonic oscillator predicts that the cross-over efficiencies between potential surfaces are greater at higher vibrational quantum numbers (67). A lowering of the zero point energy will cause the cross-over point at B (see Figure 8.) to appear at a higher vibrational level and will therefore favor the cross-over to the surface leading to Hg^0 atoms and an excited acceptor molecule. This is in agreement with the observation, that when a C-D bond is involved in the energy transfer an increase in the Hg^0 atom concentration is observed.

The exceptional behavior of neopentane seems to be related to high stabilization rate of the intermediate (see Section 1). Both modes of decomposition of the 'trapped' complex molecules appear to be important. The increased relative importance of Hg^0 formation is perhaps related to the greater number of rotational levels available.

In oxygen containing compounds the presence of an OH bond seems to be a prerequisite for Hg^0 atom formation. The high efficiency of N_2 and CO to form Hg^0 atoms is probably the result of a greater than 112 kcal bond energy; thus if a complex is

formed, it has to decompose via either Hg^0 atom formation or emission. The difference between the two molecules is the greater relative reactivity of CO molecules with Hg^0 atoms. (cf. Section 7 of this chapter).

4. A brief study of the process $\text{Hg}^1 + \text{NH}_3 \rightarrow \text{Hg}^0 + \text{NH}_3$.

It was reported earlier (68) that ammonia quenches Hg^1 atoms to the Hg^0 level, but the presence of metastable atoms were never detected experimentally.

An experimental difficulty arises from the formation of an intermediate complex between ammonia and Hg^1 atoms (54). When attempts were made to detect Hg^0 atoms with the 4047A absorption technique, an emission instead of the expected absorption was observed. It became clear that the earlier reports of the emission region 3000-3900A of $(\text{NH}_3\text{-Hg})^*$ in fact extend to longer wavelengths, and that the wing of this emission masked the expected absorption. The flash photolysis technique (30) would be subject to the same effect, since it was based on the measurement of the 2964A absorption.

It was observed that whenever metastable atoms were formed, two emission bands appeared in the emission spectrum of mercury. They were attributed to an excited, diatomic mercury molecule.

It appeared therefore, that if ammonia forms Hg^0 atoms to any appreciable extent, the observation of these emissions would confirm the quenching of Hg^1 by ammonia to the metastable Hg^0 level.

One of the excimer emission bands shows a maximum at about 4850Å and the other one at 3350Å (36). The latter emission band appears in the same spectral region as the emission from the ammonia- Hg^1 complex. Therefore it could not be used to detect the mercury excimer. In principle the other 4850Å emission can be used to detect the presence of the metastable atoms. Furthermore, it was found that the excimer emission could be effectively quenched by a small amount of NO, while the emission related to Hg^1 is relatively insensitive for the same amount of quencher. This observation provided a method for confirming whether or not the observed emission in the 4850Å region was due to Hg^0 atoms.

The experimental arrangement was described in Chapter II/2. In this study an increased flow rate was used to eliminate the interference from the reaction products.

At first the emissions were recorded using purified ammonia gas. The experiments were then repeated with

<0.1% added NO. The results are shown in Figure 24.

A large decrease in the 4850A emission intensity was observed on the addition of the quencher, while the 3350A emission band was not changed to any appreciable extent. This observation confirmed that the 4850A emission band was in fact related to the presence of Hg^0 atoms, thus proving that ammonia quenches Hg^1 atoms to the metastable level. The observation is also in agreement with the previous suggestion, that intermediate formation involves Hg^1 atoms.

5. The process $\text{Hg}^0 + \text{Hg} \xrightarrow{\text{N}_2} (\text{Hg}_2)^*$

i. Experimental arrangements and results.

There is considerable disagreement in the literature concerning the nature of the mercury molecule, and its mode of decay, although molecule formation was generally considered as a major route for the removal of Hg^0 atoms (69). Two emission bands appearing in the mercury emission spectrum were attributed to this diatomic excimer. Since the presence of Hg^0 is a prerequisite for the formation of the excimer molecule, it appeared that the detection of these emissions could be used to monitor metastable atom concentrations.

The cell and the experimental arrangement was

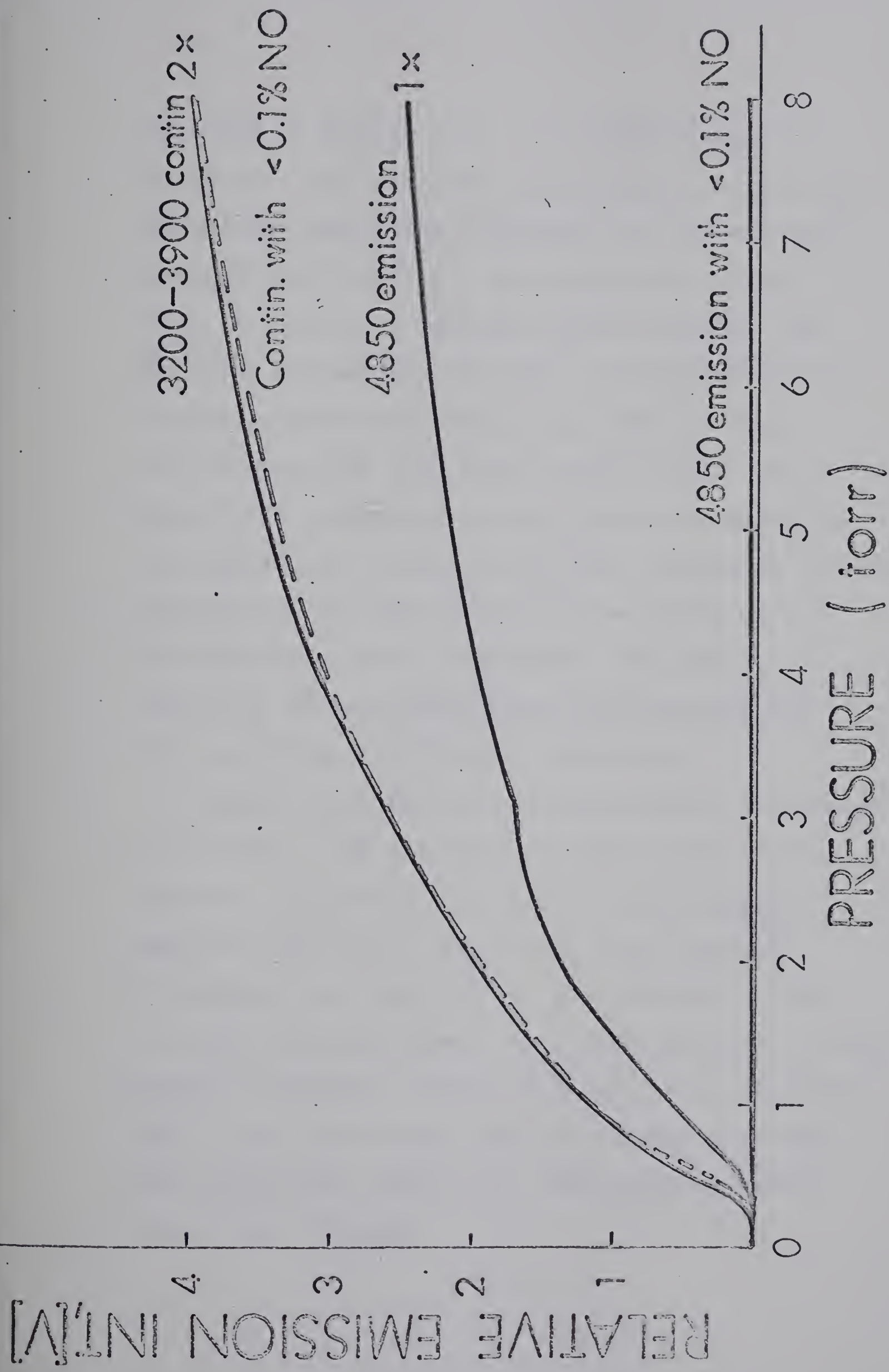


Figure 24
NH₃ emission

described in Chapter II/2. It differed from the arrangement for absorption measurements in that the 4047A light source was eliminated and the emission was monitored directly. An appropriate optical filter isolated the desired spectral region. For the lower wavelength, "b" band, a Kodak 18A + 0.5 mm Plexiglass filter was used, while the "a" band was isolated with a CR 3385 cut-off filter. An appropriate correction as been applied in quantitative comparisons to account for the difference in filter transmission and the sensitivity variation of the photomultiplier with wavelengths. The operating voltage of the photomultiplier was increased from 475V to 540V to give greater sensitivity.

Figure 25 displays both emission band intensities in nitrogen. The intensity of the "a" band varies linearly with nitrogen pressure, and the general shape of the curve is similar to that reported by Berberet and Clark (29). The variation of the "b" band intensity shows a striking similarity to the pressure dependence of the metastable atom concentration. This can be seen from the comparison of the 4047A absorption and the "b" band emission curve shown in the diagram.

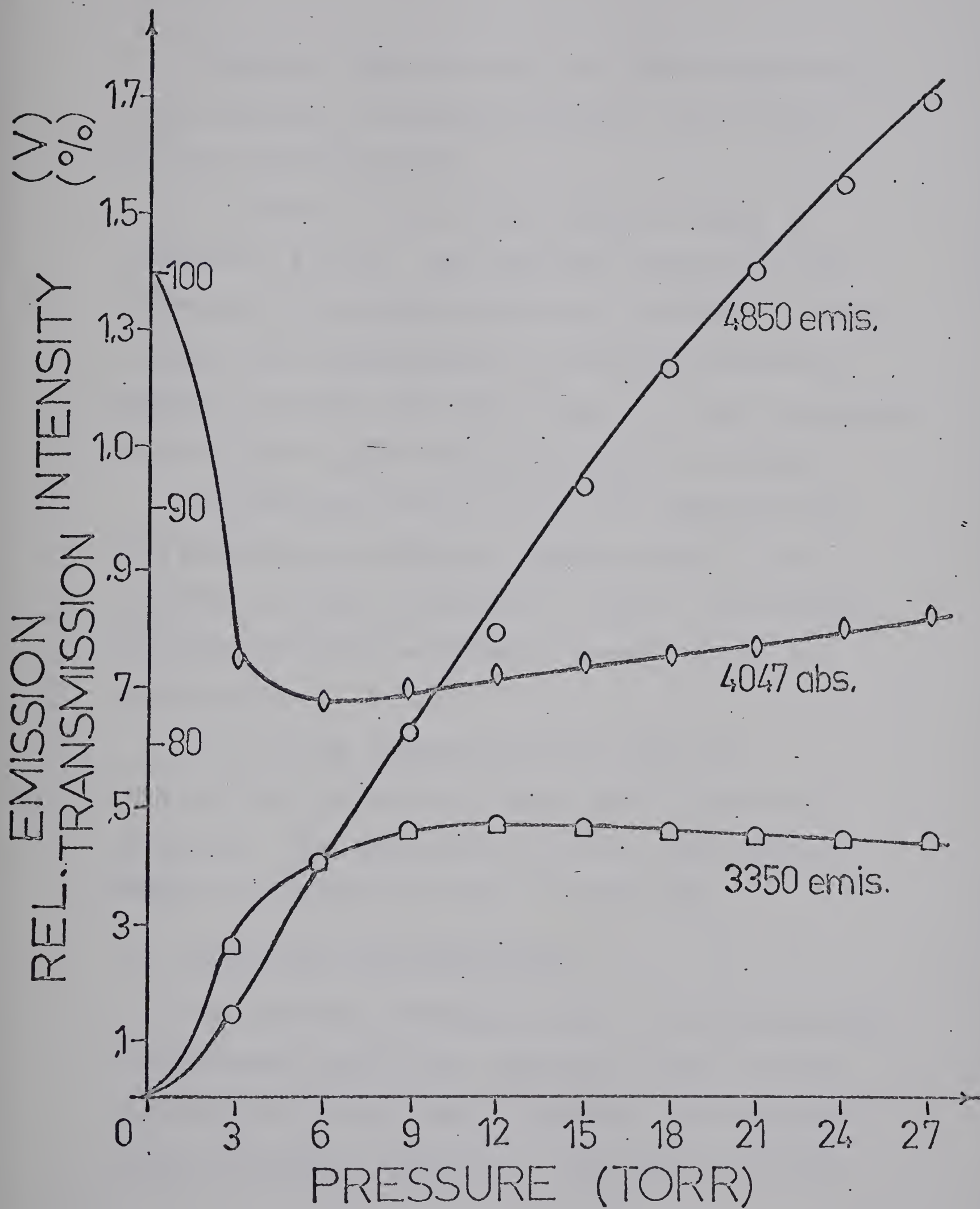


Figure 25

Mercury Nitrogen System

Figure 26 shows the ratio of the two emissions as a function of nitrogen pressure. It is linear in the region examined.

In Figures 27 to 30 the effect of added quenchers is shown. The absolute intensity of the emissions is expected to decrease, since the quencher reduces the concentration of the common reservoir. However, together with this change, a slight variation of the slope of the emission curves was noticed.

The emission ratio ("a" to "b") dependence on the pressure at different concentrations of the quencher is shown in Figures 31 and 32. The change of slope indicates a different quenching rate for each emission.

It is to be expected that not only the hydrocarbons but also nitrogen itself, quench the emissions. The experimental data for the quenching effect of nitrogen is shown in Figure 33.

ii. Discussion and Conclusions.

The emission intensity of the "b" band decreases with pressure, while the intensity of the "a" band exhibits an almost linear increase in the pressure region examined, Figure 25 . The rate of excimer

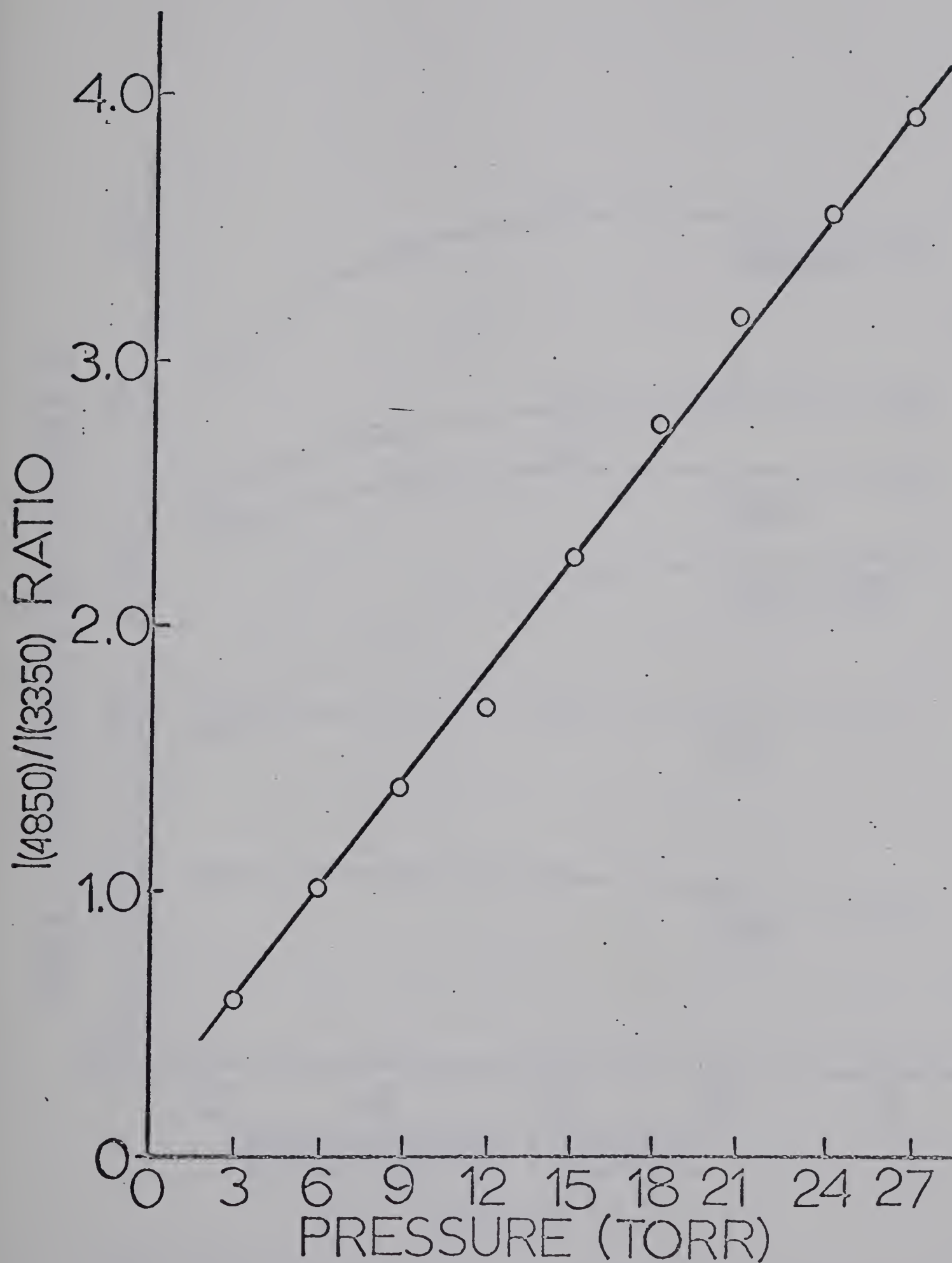


Figure 26
Emission ratios in pure nitrogen

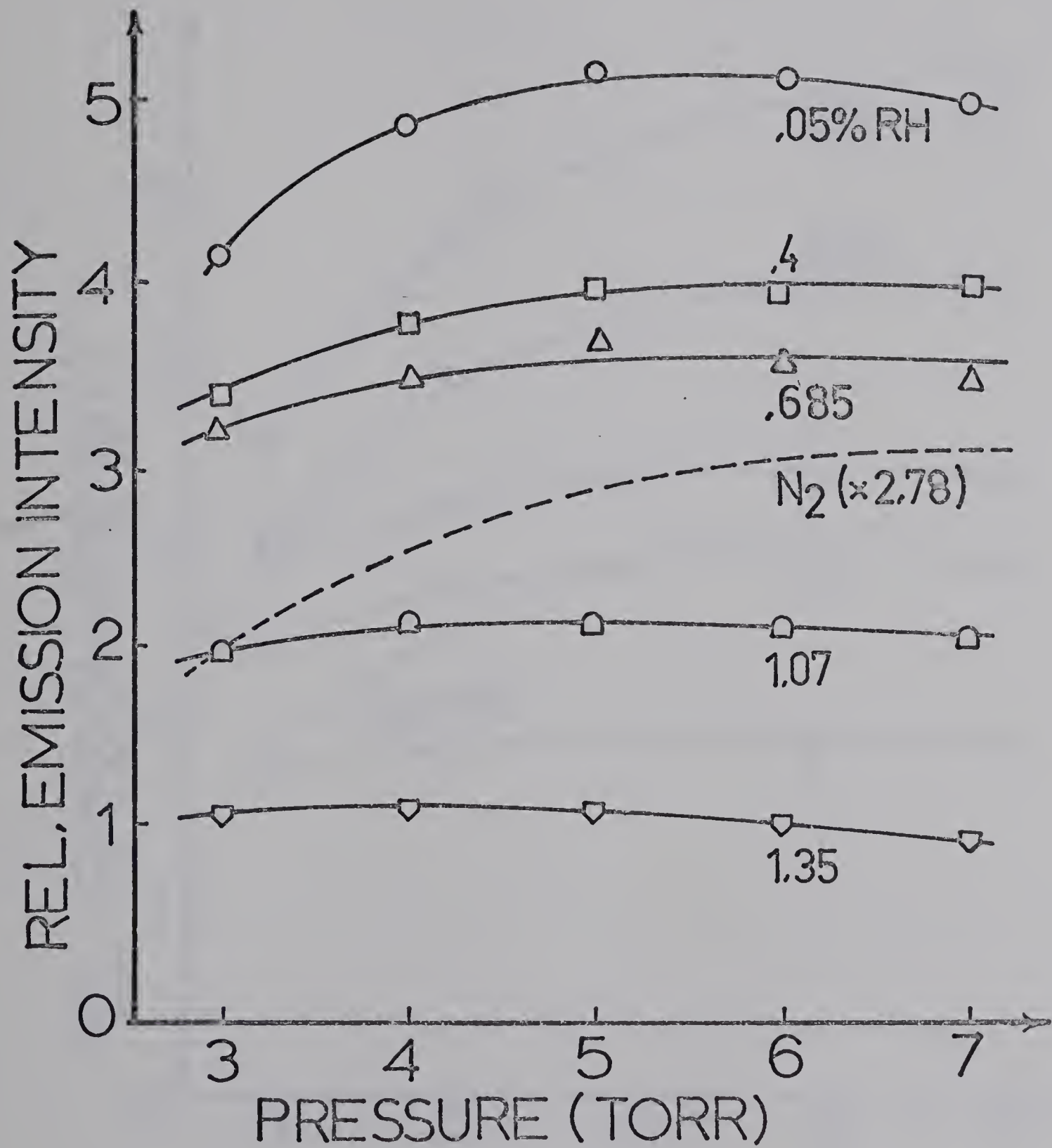


Figure 27

3350 band intensity from Nitrogen ethane mixtures

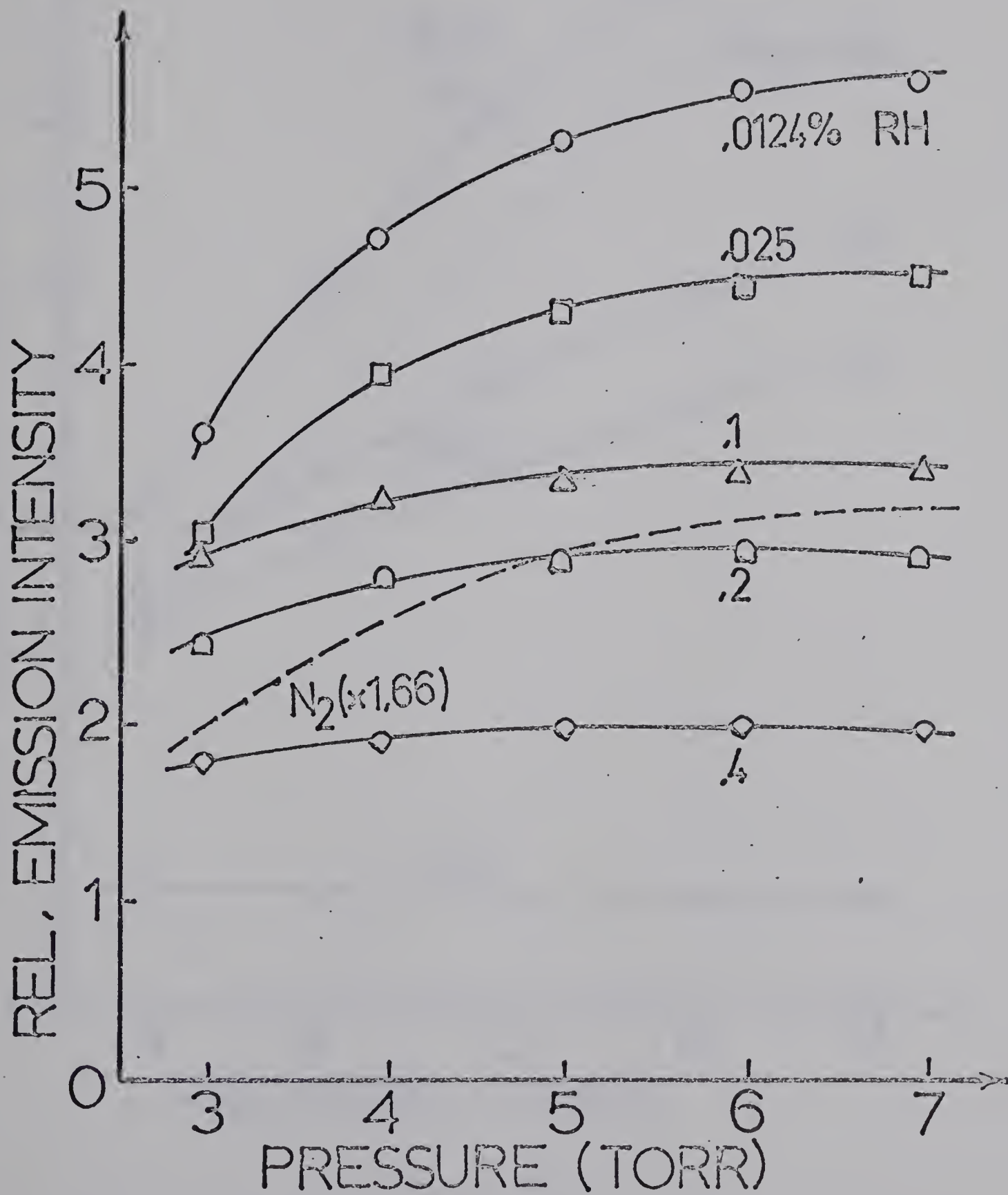


Figure 28

3350 band emission from Nitrogen-Propane mixtures

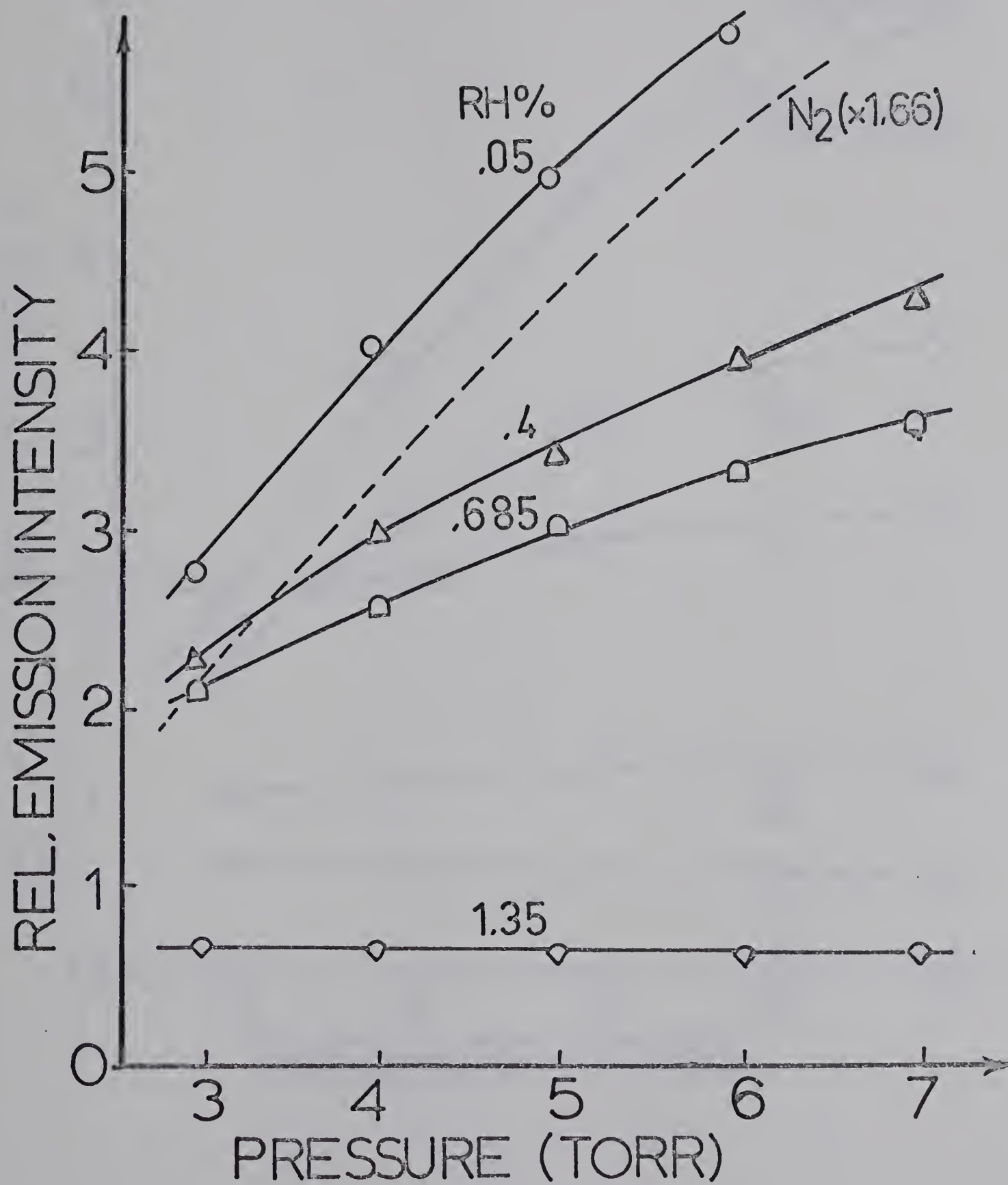


Figure 29

4850 band intensity from Nitrogen ethane mixtures

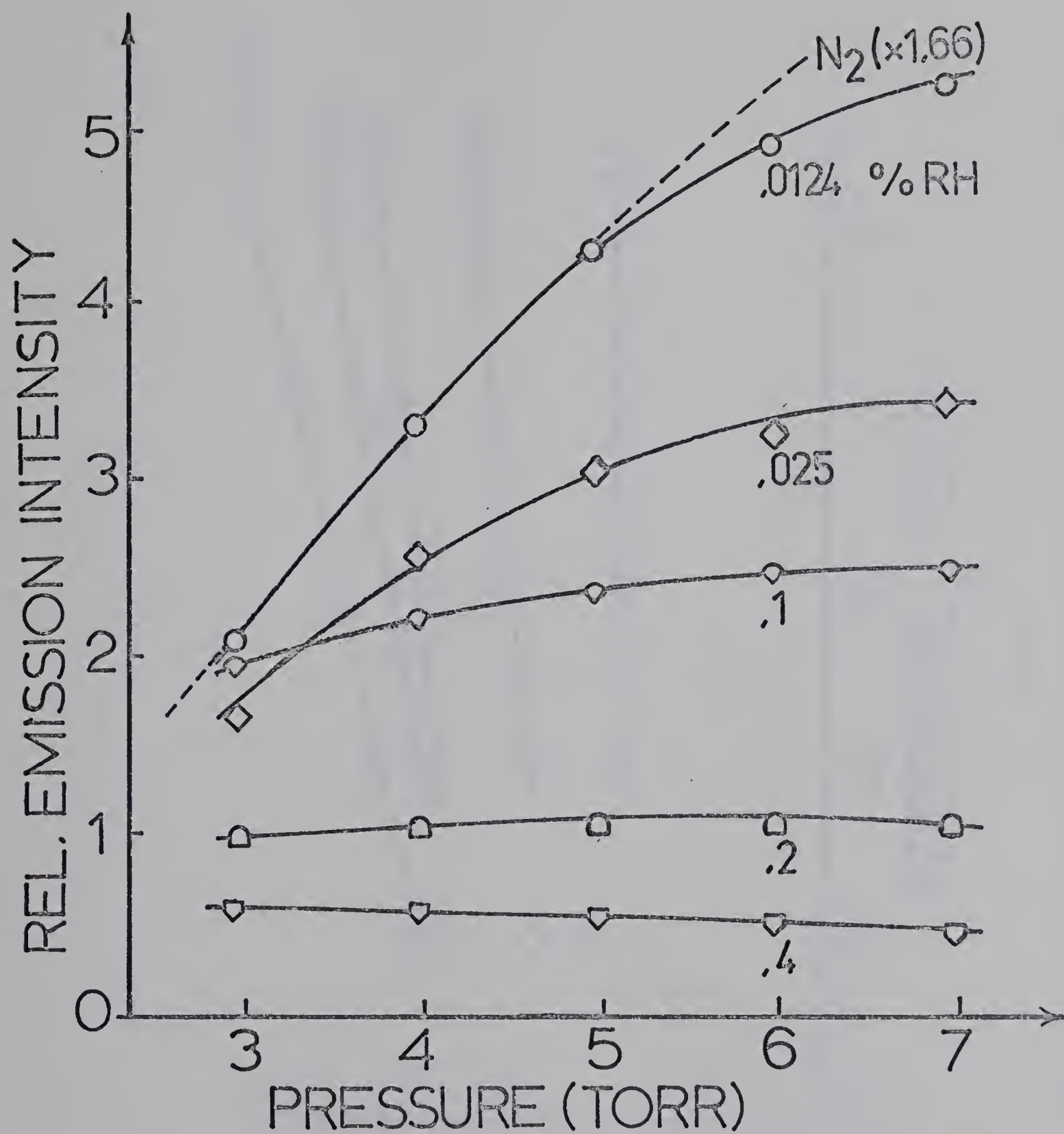


Figure 30

4850 band intensity from N₂-Propane mixtures.

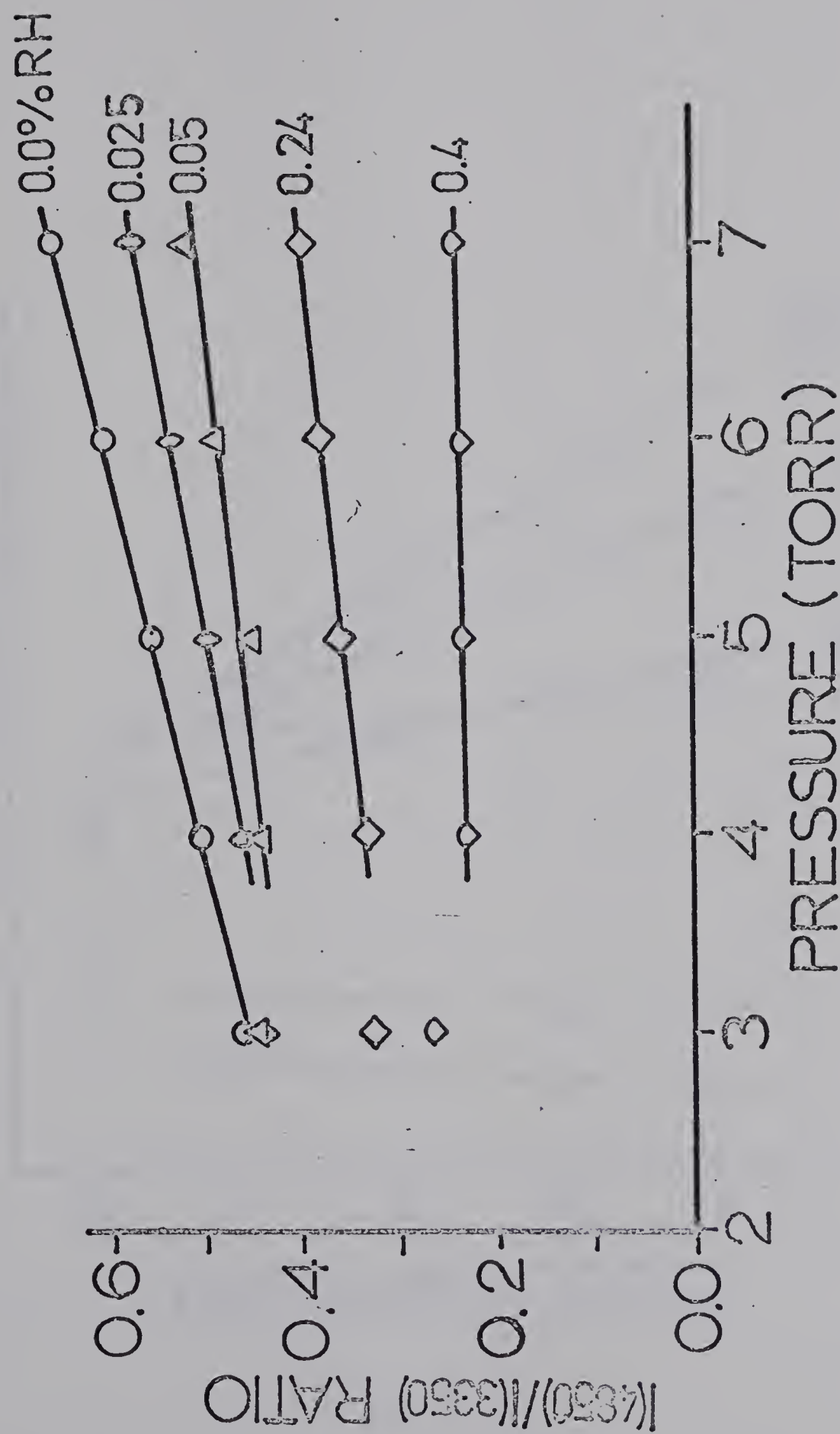


Figure 31

Emission ratios at different concentrations of ethane added to nitrogen

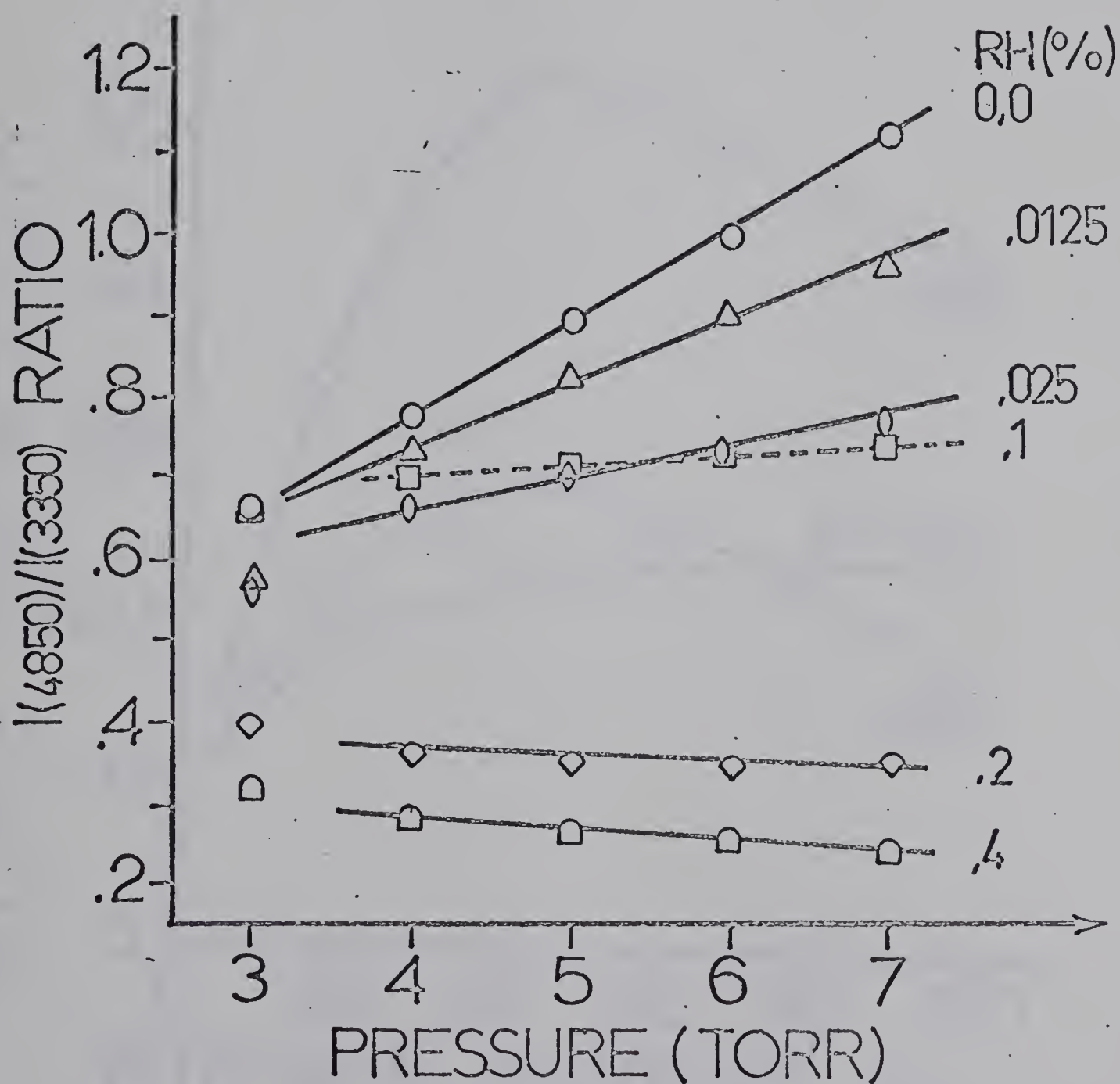


Figure 32

Emission ratios at different concentrations of propane added to nitrogen

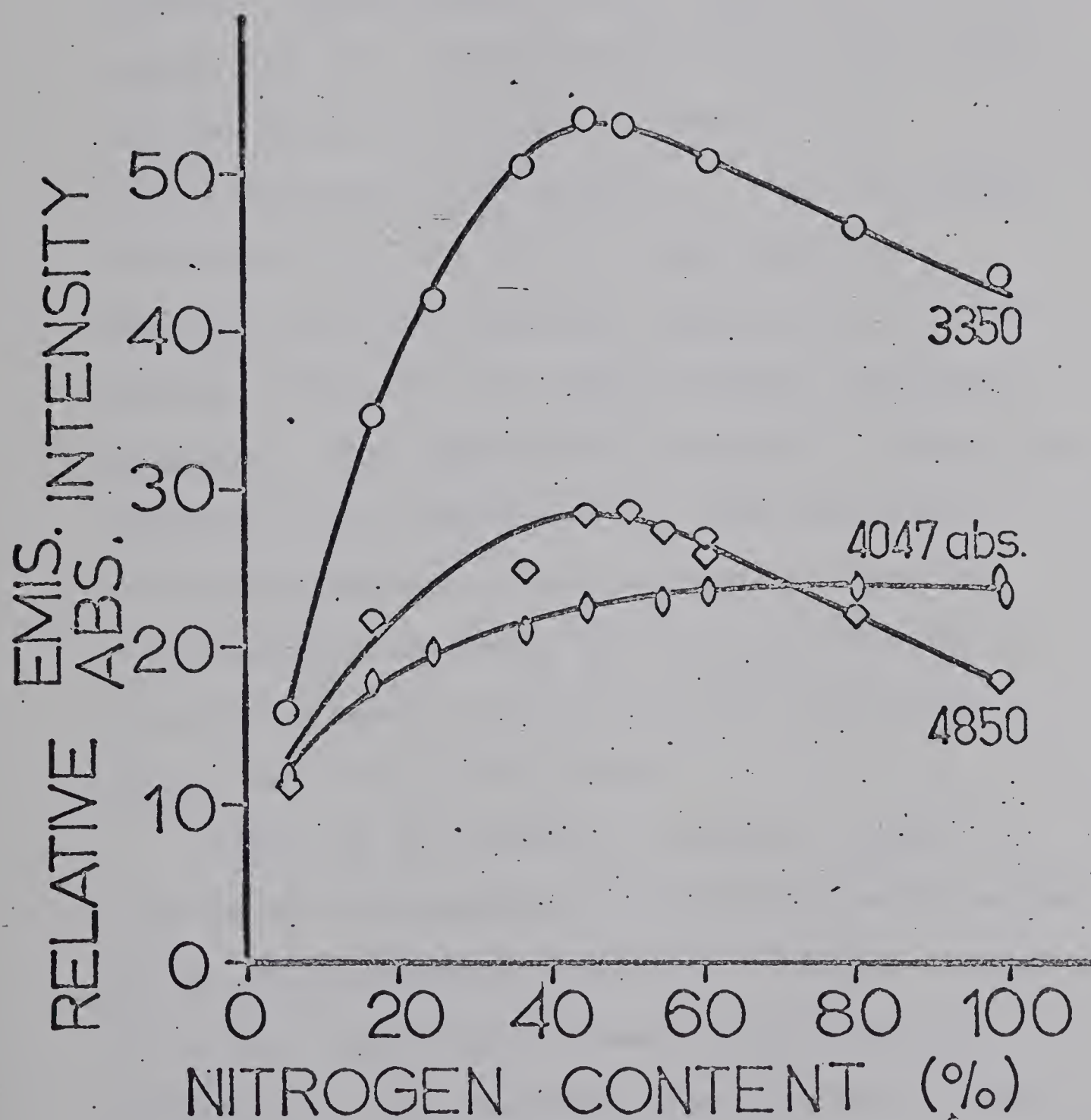


Figure 33.

Intensity variation in N_2 -Xe mixtures.
(constant pressure: 5 torr).

formation increases with pressure due to the increased rate of Hg^0 formation, and the increasing rate of stabilization of the excited Hg_2 molecule. The metastable atom reaches a constant concentration in the complete quenching region, but the stabilization of the hot initial excimer molecule capable of dissociation, always increases with pressure. The observation indicates that only the "a" band emission benefits from the increased concentration of the excimer, while the "b" band intensity decreases slightly. This observation suggests a competition reaction which favors the "a" band emission at increased pressures. The decrease of the "b" band emission intensity may be indicative of a pressure-induced conversion to the state from which the "a" band originates.

Plots of the emission intensity ratios vs. the substrate pressure at different concentrations of an added quencher, are shown in Figure 31 and 32. The plots unequivocally demonstrate that the emissions do not originate from the same excited

species. If the same excited molecule were the reservoir for the emissions, both would be quenched to the same extent by the added quencher. This would result in constant emission ratios regardless of the concentration of the quencher. However, the emission ratio varies with pressure, which can only be the result of different quenching rates for the emitting species. It would appear then; that McCoubrey's criticism (23) of the two spectroscopic states has to be rejected, since the observations strongly suggest the existence of two distinct spectroscopic levels as sources of the emission bands.

In Figure 34 Mzorowski's potential energy curves (36) for the mercury molecule are shown. The state A^3l_u is the source of the shorter wavelength "b" band emission, while the 4850Å "a" band emission originates from the $^3\Sigma_u^+$ state. At greater internuclear distances, this lower energy level changes to the $^3O_u^-$ state as a result of increasing (jj) coupling character. A cross-over of $^3\Sigma_u^-$ and 3l_u states occurs at short internuclear distances.

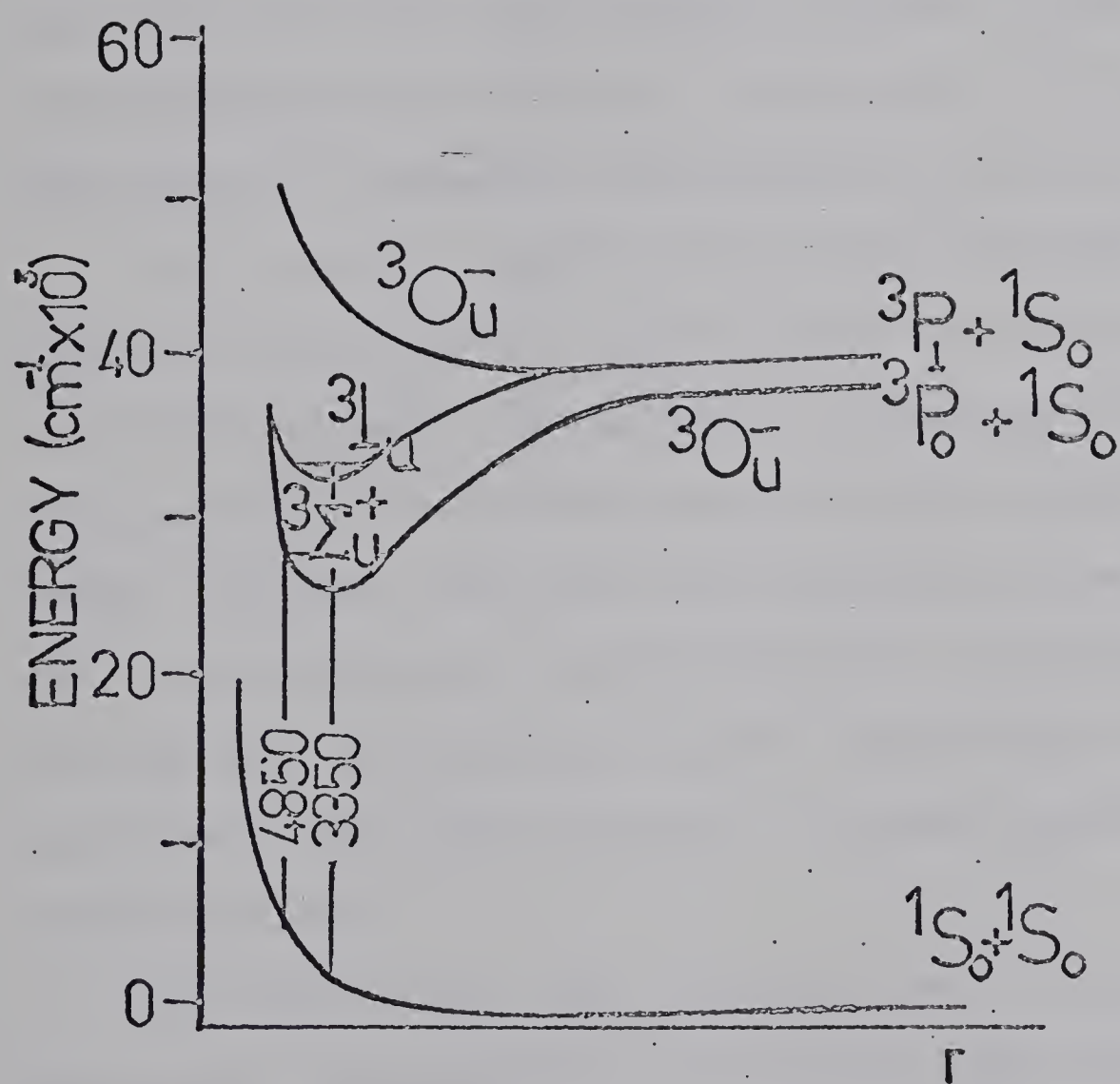


Figure 34

Hg_2 potential energy curves

When $\text{Hg}^0 + \text{Hg}$ combine the excited molecule is energetically unstable and is above the cross-over point. It goes either to the upper, or to the lower level. If a "heat sink" such as N_2 molecules is available the excimer will preferentially populate the lower electronic level. As a result, an increase of the "a" band emission intensity is observed (Figure 25). The electronic level from which the "b" band originates shows a small population decrease with pressure, presumably the result of the change in crossover efficiency with pressure (Figure 25).

The transition giving rise to the "b" band is completely allowed, but the "a" band originates from a transition allowed only at short internuclear distances. This, partially metastable character, will result in a longer lifetime, and hence the quenching of such a state will have increased probability. This is a possible interpretation of the apparent larger suppressing effect of pressure on the 4850Å emission at higher concentrations of the quencher.

The observation that nitrogen does not quench the metastable atoms does not necessarily imply that the molecule is not quenched by nitrogen. Its role in generating the emissions is very complex, since it forms Hg^0 atoms, stabilizes the excited molecule, and affects the cross-over efficiency. In addition, experiments with

added xenon, to be described below suggest that nitrogen also quenches the emissions.

Xenon did not quench Hg^1 atoms to the metastable level (Table 4). When a nitrogen-xenon mixture was used, the Hg^0 atom concentration did not decrease up to 50% Xe concentration (Figure 33), indicating that xenon did not quench the metastable atoms. At higher substitutions the Hg^0 atom concentration decreased due to incomplete quenching by nitrogen. Despite the constant value of Hg^0 concentration at less than 50% Xe, the observation was an increase of both emission intensities. It is unlikely that Xe is a better third body than nitrogen in the formation of the excimer and therefore the emission intensity increase cannot be related to the increased rate of excimer formation. The observation that the emission intensity increases must therefore be considered as the result of the reduced number of collisions by nitrogen de-activating the excimer.

When the emission ratios, $I(4850)/I(3350)$ were plotted against substrate composition, an increase of the emission ratio was noted with increasing xenon content (Figure 35). This was in agreement with the observed effect of e.g., propane substitution that the "a" band was quenched more efficiently. Despite scatter of the experimental points, a general trend can be seen in Figure 35).

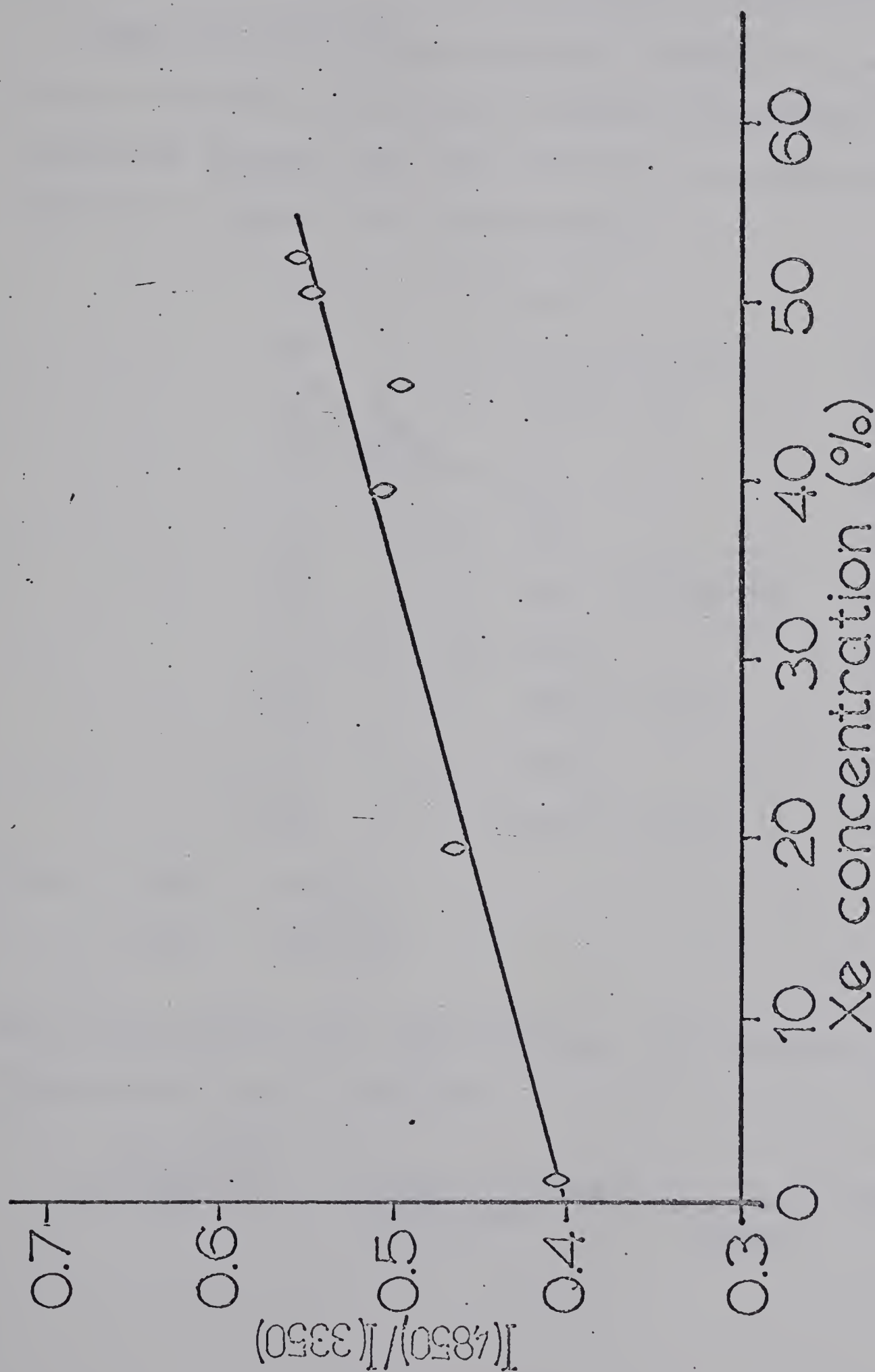
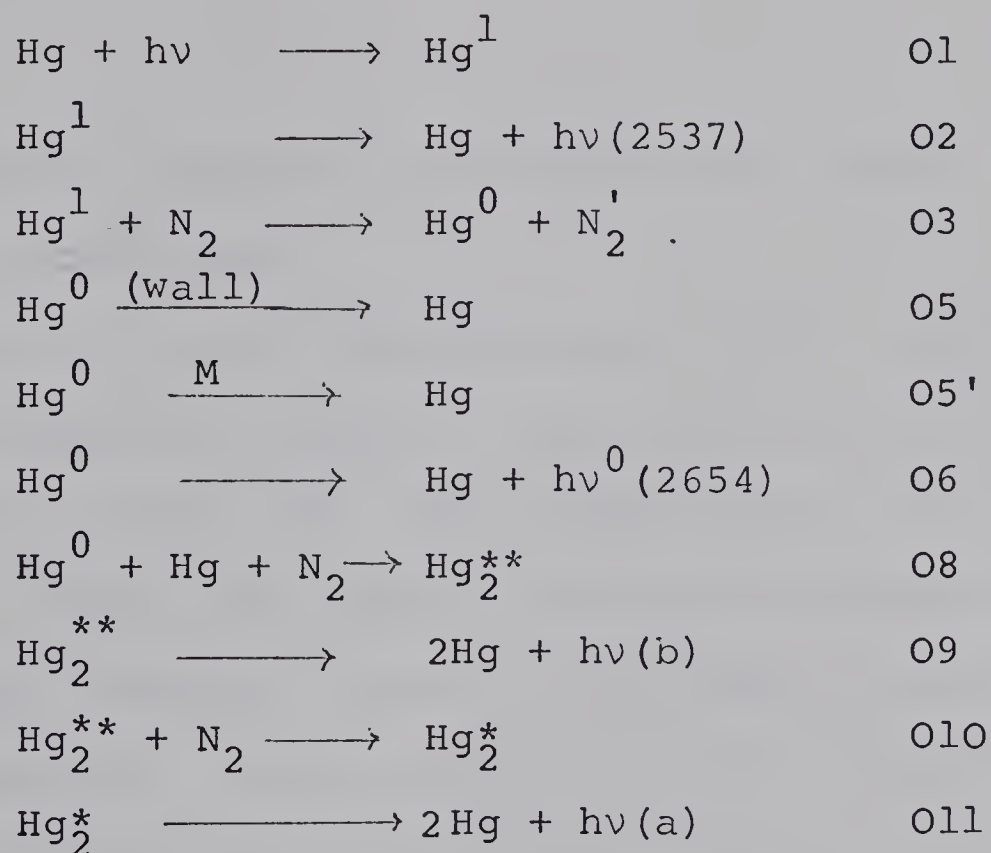


Figure 35
Emission intensity ratios at different Xe contents
(total pressure at 5 torr)

iii. The proposed reaction mechanism and the relation of nitrogen pressure to emission intensities.

Experimental evidence strongly suggests the existence of two electronic levels, and a pressure dependent internal transition between them. The following mechanism can be proposed to explain the observations;



where; $\text{Hg}_2^{**} \quad \text{Hg}_2(^31_u)$
 $\text{Hg}_2^* \quad \text{Hg}_2(^3O_u^-)$

Using the steady state approximation, the following relationships can be derived:

$$\frac{[\text{N}_2][\text{Hg}^0]}{I(b)} = \frac{k_{010}}{k_{08}k_{09}[\text{Hg}]}[\text{N}_2] + \frac{1}{k_{08}[\text{Hg}]} \quad (\text{III-9})$$

$$\frac{[N_2]^2 [Hg^0]}{I(a)} = \frac{1}{k_{08} [Hg]} [N_2] + \frac{k_{09}}{k_{08} k_{00} [Hg]} \quad (\text{III-10})$$

$$\frac{I(a)}{I(b)} = \frac{k_{010}}{k_{09}} [N_2] \quad (\text{III-11})$$

where $I(a)$ and $I(b)$ represent the 4850 and the 3350 $\text{\AA}$ emission bands respectively.

The right hand side of the Equations III-9 , III-10 and III-11 were computed (Table 5), and plotted against nitrogen pressure (Figure 36). The linearity of the plots agrees with the theory and supports the above proposed mechanism.

The emission intensity ratios vs. nitrogen pressure plot is shown in Figure 36. Theory predicts a zero intercept, while the experimental curve gives the relatively small value of 0.1. The slope of this line is k_{010}/k_{09} (see Equation III-11). It has the experimental value of 0.14 mm^{-1} . The radiative lifetime (k_{09}) of Hg_2^{**} was suggested by McCoubrey (23) to be about 1×10^{-7} sec. Hence from the value of the slope, k_{010} is calculated to be about $6.6 \times 10^{-14} \text{ molec.}^{-1} \text{ sec.}^{-1}$. This value corresponds to approximately one out of every four collisions being effective in initiating the transition.

TABLE 5

Tabulation of data obtained for the N₂-Hg system

(Values are given in relative units)

N ₂ pressure (torr)	3	6	9	12	15	18	21	24	27
corr. factor	0.41	0.58	0.68	0.74	0.78	0.81	0.84	0.85	0.86
(Hg ⁰)	8.0	8.6	8.2	8.1	7.7	7.7	7.3	7.1	6.8
(Hg ⁰) _{corr.}	3.3	5.0	5.6	6.0	6.0	6.2	6.2	6.1	5.9
I(b)	26	41	45	46	45	45	44	44	43
I(a)	15	41	62	79	104	124	140	155	169
I(a)/I(b)	0.57	1.00	1.38	1.71	2.28	2.78	3.19	3.54	3.92
$\frac{(\text{Hg}^0)(\text{N}_2)}{\text{I(b)}}$	0.92	1.35	1.66	2.10	2.55	3.11	3.50	3.89	4.26
$\frac{(\text{Hg}^0)(\text{N}_2)^2}{\text{I(b)}}$	0.48	0.76	1.06	1.48	1.67	2.01	2.31	2.64	2.92

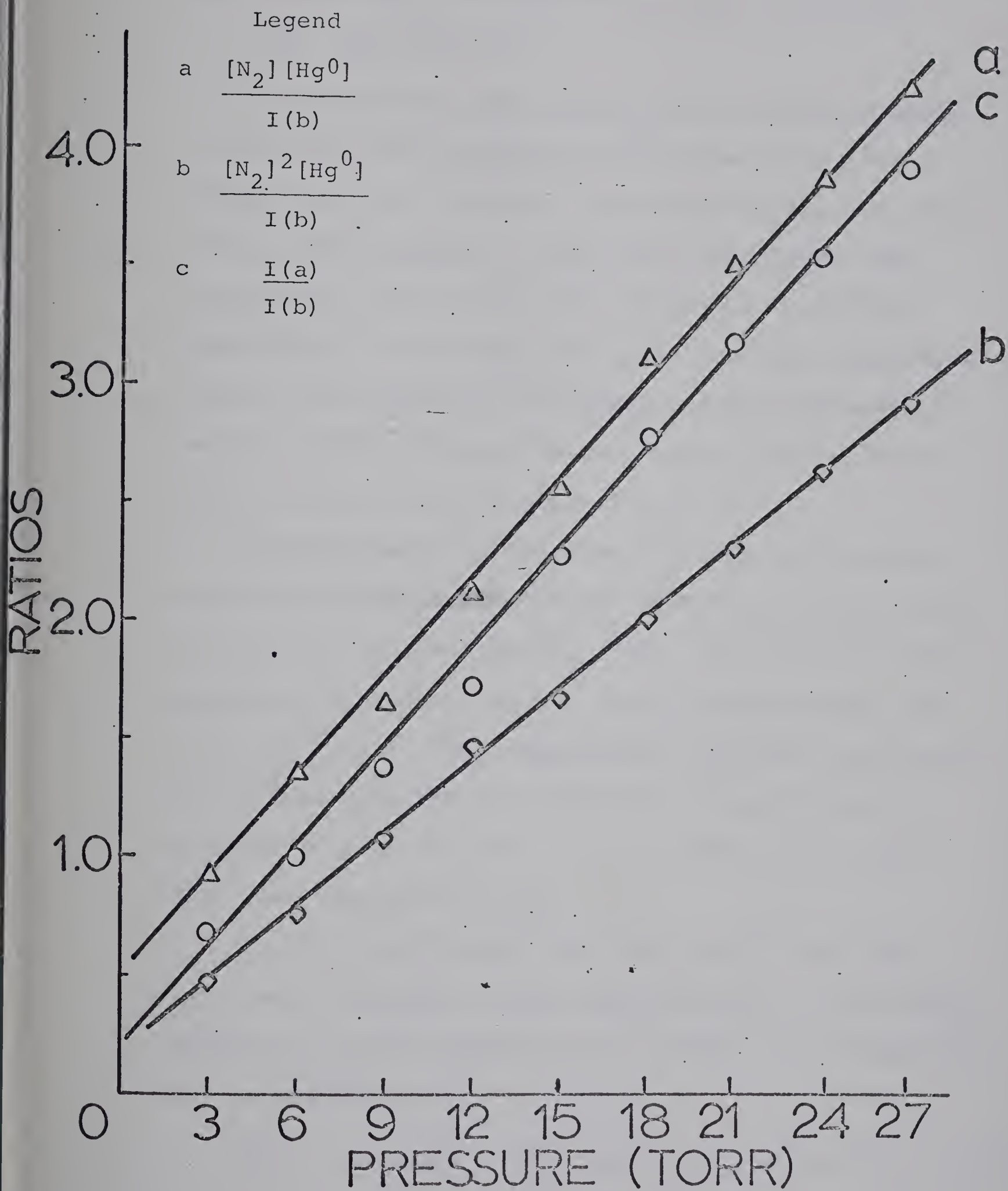
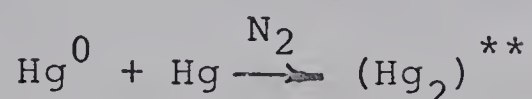


Figure 36

N_2 pressure vs. theoretical emission relationships

iv. Calculation of rate constant for the process



A relatively simple mechanism was proposed above to describe the formation of Hg^0 atoms and Hg_2^{**} excimer in pure nitrogen. An earlier attempt by LeRoy et al. (69) to derive a rate for this process (08) yielded the third order rate constant, $\sim 1.10^{-27} \text{cc}^2 \cdot \text{molec}^{-2} \cdot \text{sec}^{-1}$ which appeared to be too high. McCoubrey's value (23), obtained from emission decay measurements was $1 \times 10^{-30} \text{cc}^2 \cdot \text{molec}^{-2} \cdot \text{sec}^{-1}$ which differed from that of LeRoy's by a factor of 10^3 .

The following calculation is based on the above proposed mechanism and the previously published values of k_{03} (11) k_{05} (37) and k_{06} (26). The mercury vapour pressure (determined by the ambient temperature) was 1.2×10^{-3} torr. The imprisonment lifetime was corrected for the experimental conditions using Holstein's formula (as given in Eq.I-3). The value of $0.9 \times 10^6 \text{sec}^{-1}$ was obtained for k_{02} .

In the steady state, the rate of Hg^0 atom formation must be equal to the combined rates of its decay. From the proposed mechanism, the steady state expression may be written as:

$$(\text{I}_a^0)_\alpha = k_{06} (\text{Hg}^0)_\alpha + \frac{k_{05}}{\alpha} (\text{Hg}^0)_\alpha + k_{08} (\text{Hg}) (\text{Hg}^0)_\alpha (\alpha) \quad (\text{III-12})$$

where α denotes a pressure.

I_a^0 the rate of formation of the metastable atoms.

(For derivation of this equation see Appendix 1).

The relative values of the Hg^0 atom concentration which appear in this expression were determined from the 4047A absorption measurement. The initial value of the metastable atom concentration is governed by the competition of reactions (02) and (03). This value cannot be determined directly, but can be obtained from a knowledge of the correction factors for the absorption intensity at each pressure. The correction factor, $\underline{f}$, is given by

$$\underline{f} = \frac{k_{03}P(N_2)}{k_{02} + k_{03}P(N_2)} \quad (III-13)$$

The calculated values for $\underline{f}$ at different pressures are given in Table 5 with the corrected values for Hg^0 atom concentration.

Since

$$(I_a^0)_\beta = \frac{\underline{f}(\beta)}{\underline{f}(\alpha)} (I_a^0)_\alpha \quad (III-14)$$

and considering the ratio of Eq. III-12 at pressures α and β

$$R = \frac{k_{06} + k_{05}/P_\alpha + k_{08}(Hg)P_\alpha}{k_{06} + k_{05}/P_\beta + k_{08}(Hg)P_\beta} \times \frac{(Hg^0)_\alpha}{(Hg^0)_\beta} \quad (III-15)$$

where:

$R=f(\alpha)/f(\beta)$ can be calculated from values of f at different pressures.

The values of $(\text{Hg}^0)_\alpha$ and $(\text{Hg}^0)_\beta$ are the corrected values of the metastable atom concentration at pressures α and β (Table 5).

Therefore the only unknown, k_{08} , can be calculated from the above equation.

Considering different values for α and β , the average of eight different combinations yielded:

$$3.31 \times 10^3 \text{ mm}^{-2} \cdot \text{sec.}^{-1} \text{ or } 3.06 \times 10^{-30} \text{ cc.}^2 \text{ molec.}^{-2} \text{ sec.}^{-1}$$

The average variation of the latter figure was ± 0.28 for the eight computed values. However it should be noted that the actual rate constant error is much greater due to the errors in the adopted values of k_{05} and k_{03} .

An alternative method can also be used to calculate the third order rate constant. The steady state treatment, relating the 2537A exciting light intensity and the nitrogen pressure to the Hg^0 atom concentration, yields;

$$\left(\frac{I_a}{(\text{Hg}^0)_r} \right) = \frac{k_{05}k_{02}}{k_{03}(\text{N}_2)^2} + \frac{k_{02}k_{06}}{k_{03}(\text{N}_2)} + \frac{k_{08}k_{02}}{k_{03}}(\text{Hg}) + \frac{k_{05}}{(\text{N}_2)} + \frac{k_{06} + k_{08}(\text{Hg})(\text{N}_2)}{k_{03}} \quad (\text{III-16})$$

(For derivation see Appendix I.) The expression has a minimum, and the dependence of $\left(I_a / (\text{Hg}^0) \right)_r$ becomes linear

with increasing pressure. The minimum value occurs when

$$\frac{d(\text{Ia}/\text{Hg}^0)}{d(\text{N}_2)} = 0 \quad (\text{III-17})$$

The derivative of the Eq. III-12 after rearrangement yields

$$k_{08}(\text{Hg})(\text{N}_2)_m^3 - \frac{k_{02}k_{05}}{k_{03}} + k_{05}(\text{N}_2)_m - \frac{2k_{02}k_{05}}{k_{03}} = 0 \quad (\text{III-18})$$

Substituting the known values and rearranging for k_{08} :

$$k_{08} = \frac{7.86 \times 10^2 (\text{N}_2)_m + 1.77 \times 10^3}{(\text{N}_2)_m^3 (\text{Hg})} \quad (\text{III-19})$$

The minimum value of Hg^0 atom concentration occurs at approximately 7 torr (Figure 25). Using Eq. III-19 the value of k_{08} is found to be

$$1.84 \times 10^4 \text{ mm.}^{-2} \text{ sec.}^{-1} \text{ or } 1.71 \times 10^{-29} \text{ cc.}^2 \text{ molec.}^{-2} \text{ sec.}^{-1}$$

The value obtained from this treatment is 5.6 times greater than that obtained from the steady state treatment for Hg^0 atoms. It is evident from an examination of Figure 25 that the minimum pressure value is not well defined. The error arising from

this source is significant, since the expression involves the third power of the minimum pressure value. The error in the adopted literature values will influence the final result differently in each method. The approach based on the derivative method makes use of a single experimental result, and is therefore subject to a greater experimental error than the alternative steady state treatment.

The numerical results of the two methods are within the expected limits of a third order rate order constant, but more confidence may be placed on the value derived from the steady state treatment, $3.06 \times 10^{-30} \text{ cc}^2 \text{ molec.}^{-2} \text{ sec.}^{-1}$. It is this value that has been used in calculations described later in this thesis.

The eight values obtained from the steady state treatment described above are in good agreement with one another. Their average is consistent with the value obtained by the derivative method and that reported by McCoubrey (23). This shows that the reaction mechanism describes the observations well.

6. The mercury excimer emissions from H_2O and D_2O systems.

It was reported by Gaviola and Wood (54) that

water vapor emits from mercury photosensitized systems. This emission was attributed to the formation of an intermediate, $(\text{Hg.H}_2\text{O})^*$, formed from Hg^1 atoms. Emissions were reported from a number of other photosensitized systems, but water is unique in that its emission is several times stronger than hydrocarbons and has a wider spectral range than other compounds.

The formation of Hg^0 atoms in water vapor-mercury systems was confirmed by measuring the 4047A absorption. Some doubt arose concerning the validity of the absorption measurements, because of the possible interference from a reaction product. The emission bands of the excimer presented a suitable means of detecting Hg^0 atoms, but the emission attributed to the $(\text{Hg.H}_2\text{O})^*$ complex was a source of interference which had to be taken into account.

The measuring system for the 4047A absorption, and the excimer emission studies were described in Chapter II/2. The emission from the complex $(\text{Hg.H}_2\text{O})^*$ was examined using 2800A and 3100A interference filters.

Triple distilled water, and Merck and Sharp reagent grade D_2O , were used in these experiments. The isotopic purity of the latter was reported to be better than 99%. Both compounds were purified by low temperature bulb to bulb distillation.

The measurements required the higher water vapor flow rate of approximately 30cm/sec. to prevent the retention of any products in the illuminated zone. Maintaining a constant flow during the runs presented some experimental difficulties. The reservoir pressure decreased during the run because of the increased flow rate and the slow evaporation rate of liquid water. Frequent heating of the water reservoir and manual adjustment of the flow regulators decreased the variation, but it remained the largest single source of error.

Figure 37 and 38 display the absorption and various emissions for H_2O and D_2O - mercury systems.

The 4047A absorption curves indicate that both systems are almost equally efficient in producing metastable atoms. A difference becomes noticeable at increasing pressures, namely, that the Hg^0 atom concentration decreases faster in light water.

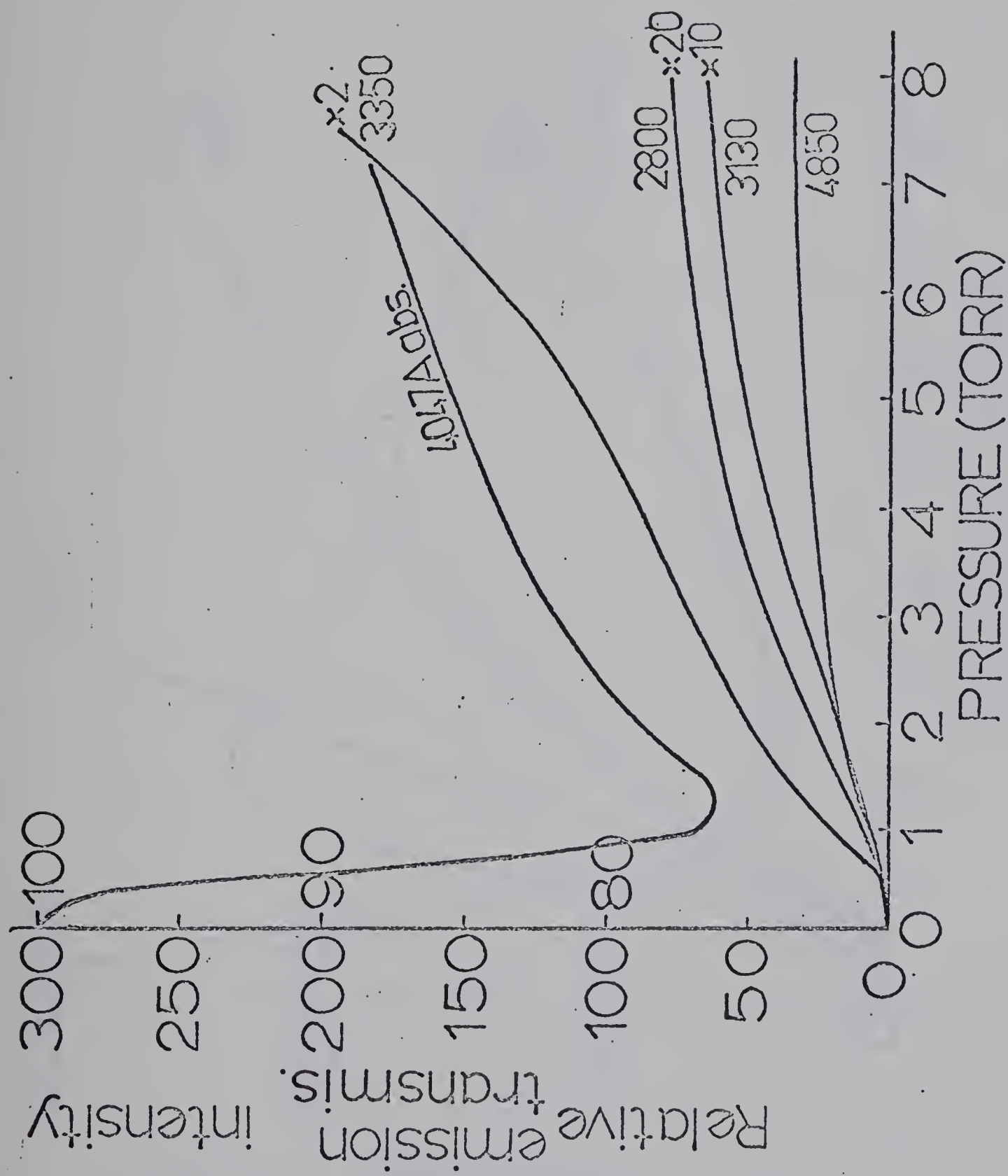


Figure 37

H₂O-Hg system

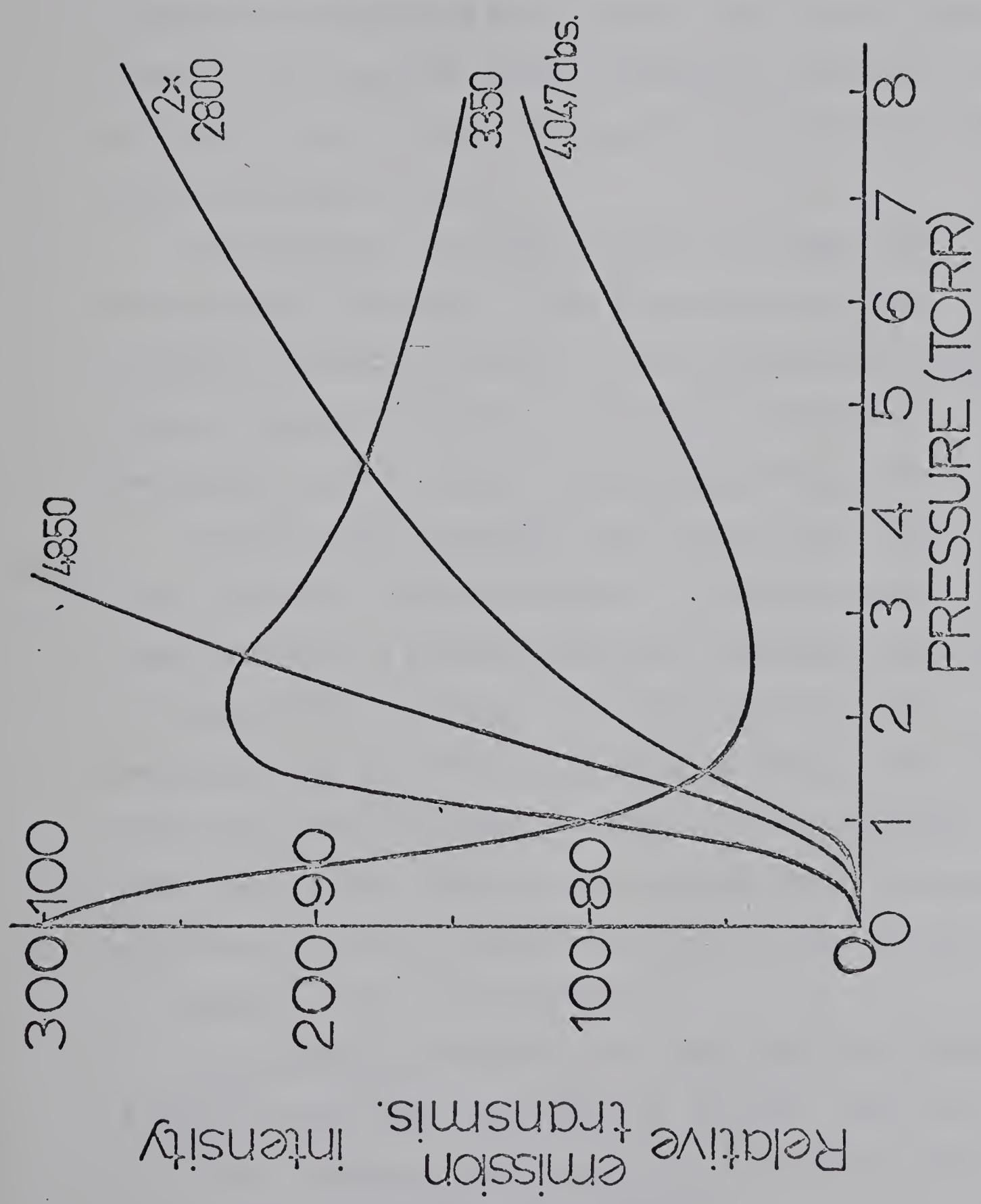


Figure 38.
Hg - D₂O system.

The "a" band emission intensity is greater from D_2O than from H_2O , but the Hg^0 atom concentration profile is similar in both cases. This may be attributed to the superior energy accepting properties of the heavy water, thus favoring the transition to the lower electronic level.

The emission intensity of the "b" band shows the expected behavior in the heavy water system. It reaches a maximum at about 2 torr pressure and then shows a constant decline. The ratio of the two emissions shows a linear relationship (Figure 39).

The "b" band emission from light water differs from all other examined systems. The photosensitized vapor exhibits a strong emission continuum commencing at about 3100Å. However, the emission intensity measured with the 3100Å interference filter was still about half that recorded at 2800Å. This indicates that the emission wing extends beyond 3100Å, and that it may be sufficiently intense at the "b" band region to interfere with the observations.

The emission observed with the 2800Å interference filter for H_2O was approximately 8 times that for D_2O at 5 torr pressure. No emission was detected with the 3100Å interference filter for D_2O .

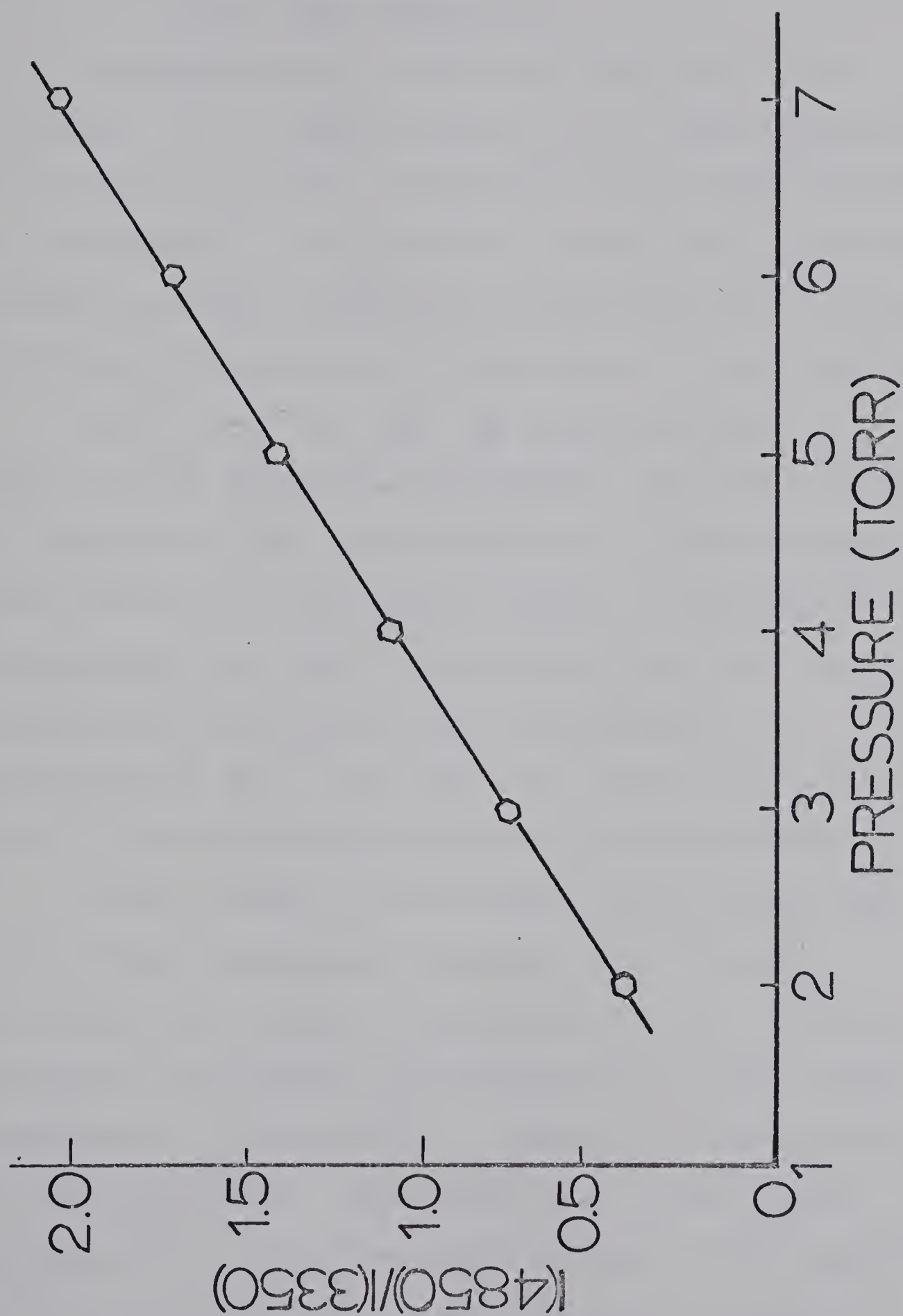


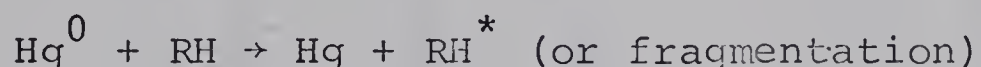
Figure 39

Emission ratio in Hg-D₂O system

7. The process $\text{Hg}^0 \xrightarrow{\text{A}} \text{Hg}$.

(i) Results and discussion.

The compounds to be examined were mixed with nitrogen. It was assumed that the Hg^0 atom formation was due only to nitrogen, and that the added compound acted as deactivator of the metastable atoms. The difference between the 4047A absorption intensity of pure nitrogen and that of the mixture was attributed to the reaction



Prior to each absorption measurement from the mixtures an absorption curve was recorded with pure nitrogen, which served as a reference standard. The absorption measurements for pure nitrogen were made under such experimental conditions that the absorption was approximately 20%. This value was chosen since it fell in the range where Beer's law is obeyed (29).

A large number of measurements were carried out using ethane and propane mixtures with nitrogen. The results are shown in Figure 40 and 41. The points marked on the diagrams are averages of at least three measurements, corrected for a common arbitrary reading for nitrogen alone. The dashed part of the curves are intended to show the general shape in this region.

The addition of various deuterated propanes to nitrogen, and their effect on the 4047A absorption is

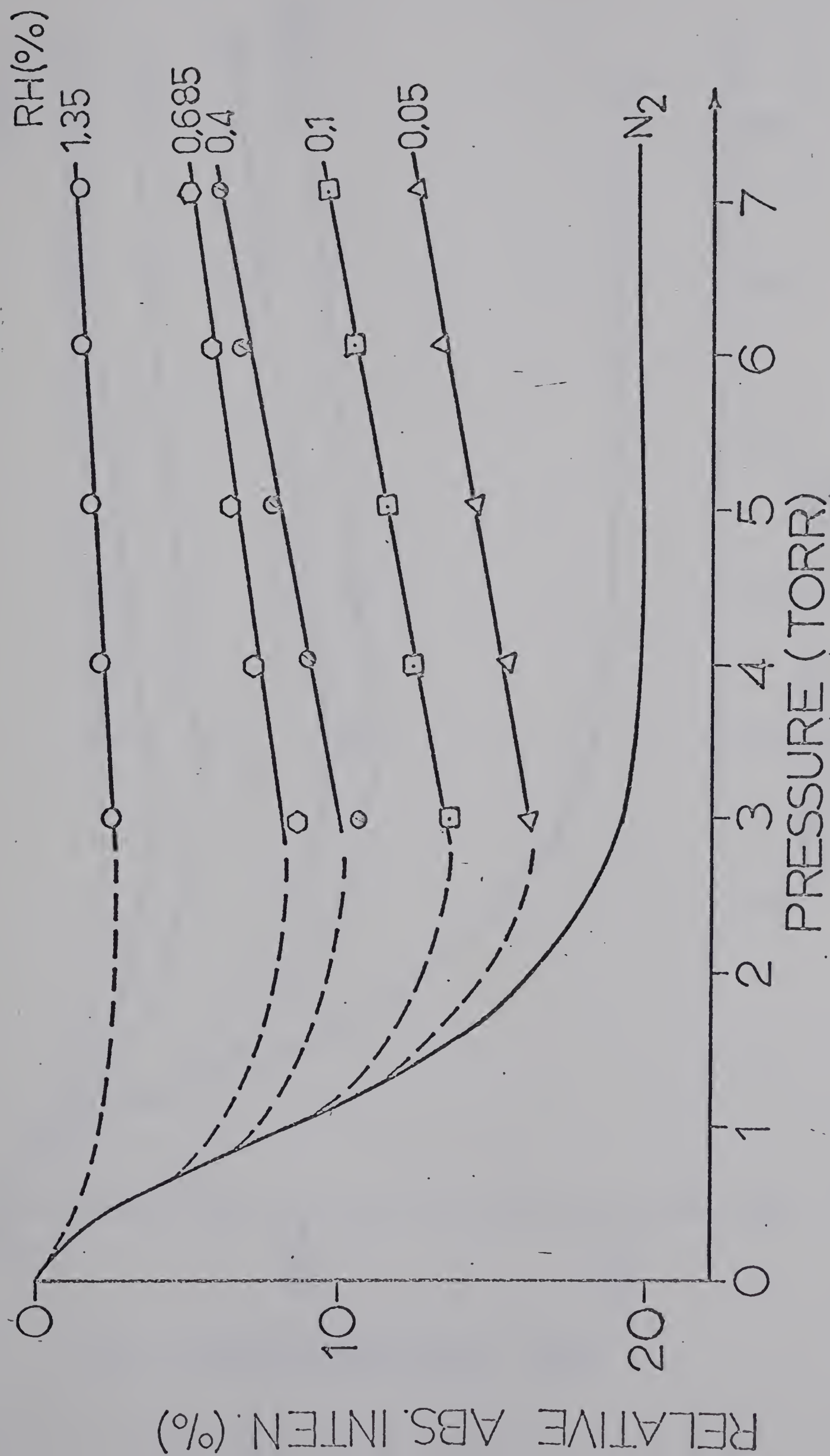


Figure 40.4047A Absorption intensity in nitrogen ethane mixtures.

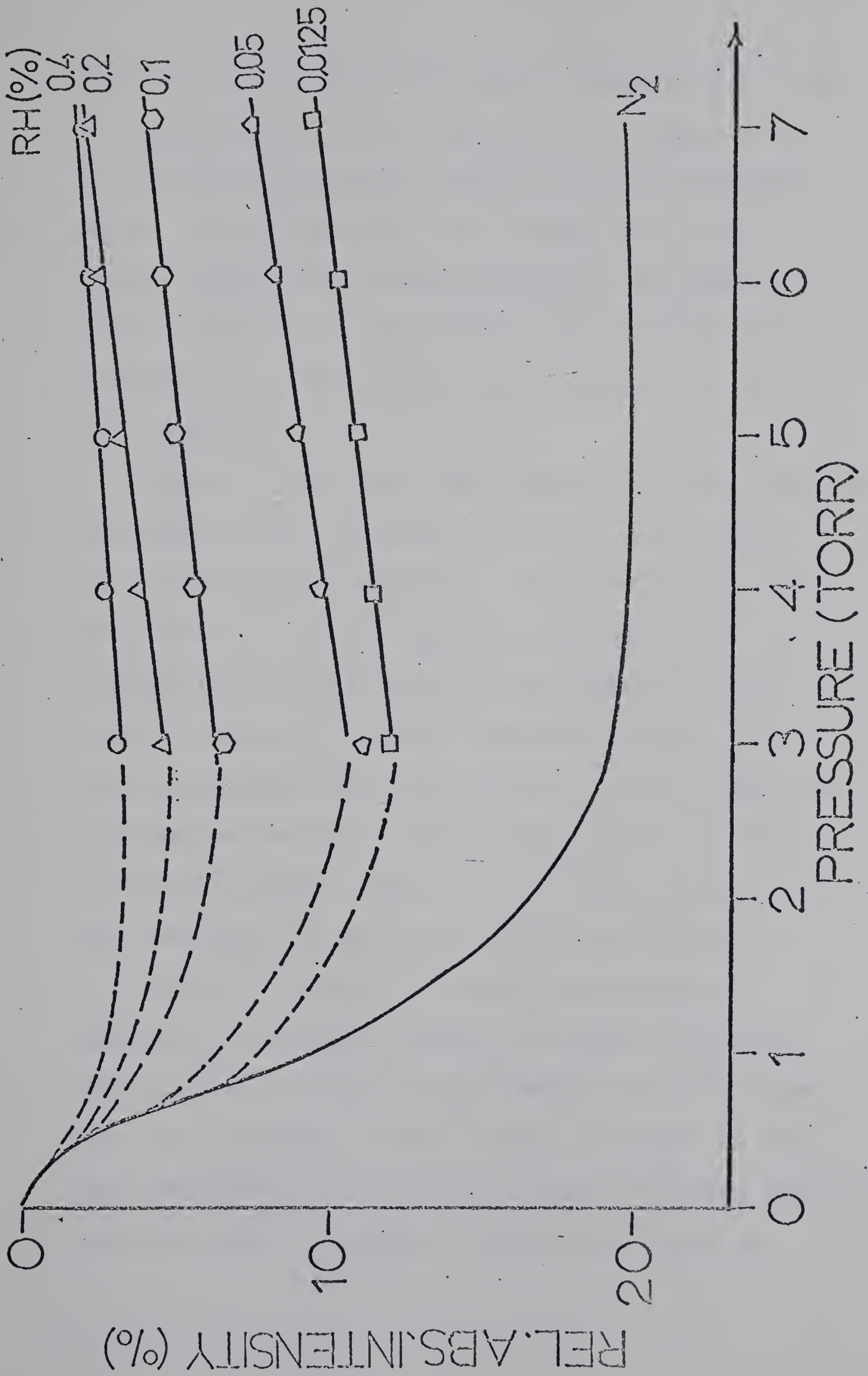


Figure 41. 4047A Absorption Intensity in Nitrogen Propane Mixtures.

shown in Figure 42. The largest decrease from pure nitrogen absorption was observed with C_3H_8 , while the deuterated propanes exhibit a lower quenching rate. Concurrent with this effect there was a higher steady state concentration of Hg^0 atoms in those propanes (in the absence of nitrogen) which produced the lowest rate of metastable atom removal (cf. Figure 19).

Table 6 shows both the physical and the chemical quenching cross sections, and their ratios for various deuterated propanes. The last column lists the ratios of the Hg^0 concentration decrease. It is noticeable that the ratios of Hg^0 removal rates are closer to those of the Hg^1 quenching cross section ratios obtained from the physical, rather than from the chemical method. These values show that there is kinetic isotope effect for Hg^0 atoms similar to that obtained for Hg^1 by the physical method.

Figure 43 shows the effect of neopentane addition to nitrogen compared to that of propane. Their relative rates of Hg^0 removal and their quenching cross sections for Hg^1 atoms are shown in Table 7. Both compounds have a similar quenching cross section value for Hg^1 , but their rates of Hg^0 removal

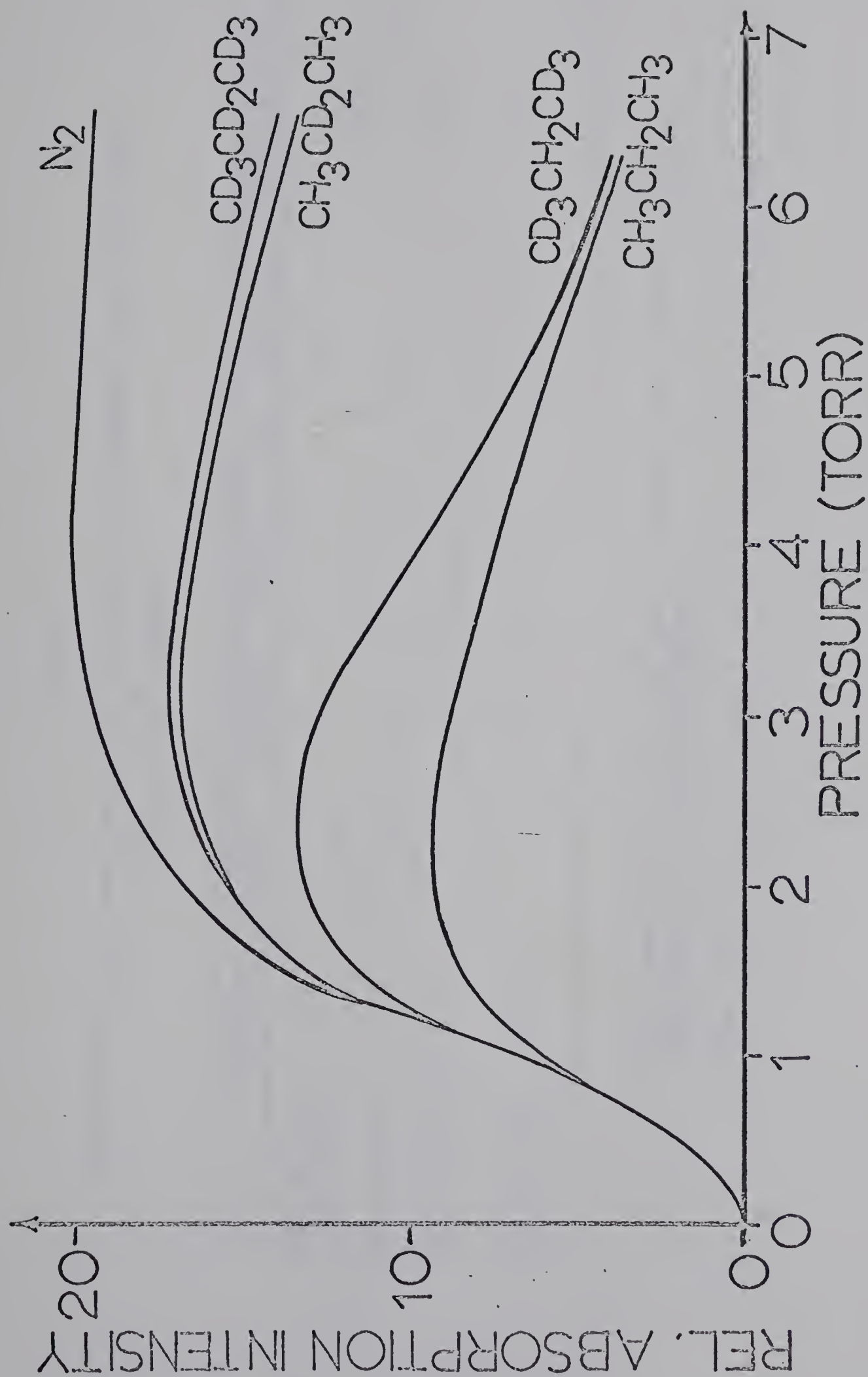


Figure 42. 4047A absorption from 0.1% Propane- N_2 mixtures

TABLE 6

Quenching cross section relationships of propanes obtained for
 Hg^1 and Hg^0 atoms.*

	Chemical	Quenching Ratio	Cross Physical	Sections Ratio	Rel.value of Hg^0 conc. decrease	Ratio of Hg^0 conc.decrease
$\text{CH}_3\text{CH}_2\text{CH}_3$	1.7	1.23	1.7	1.22	7.1	1.08
$\text{CD}_3\text{CH}_2\text{CD}_3$	1.4	7.09	1.4		6.6	3.08
$\text{CH}_3\text{CD}_2\text{CH}_3$	0.24	13.1	0.59	2.88	2.3	3.40
$\text{CD}_3\text{CD}_2\text{CD}_3$	0.13		0.47	3.62	2.1	

* The measurements for Hg^0 was carried out from 0.1% RH-N_2 mixtures at 5 torr pressure.

The pure nitrogen reading under the same condition was 19.9%.

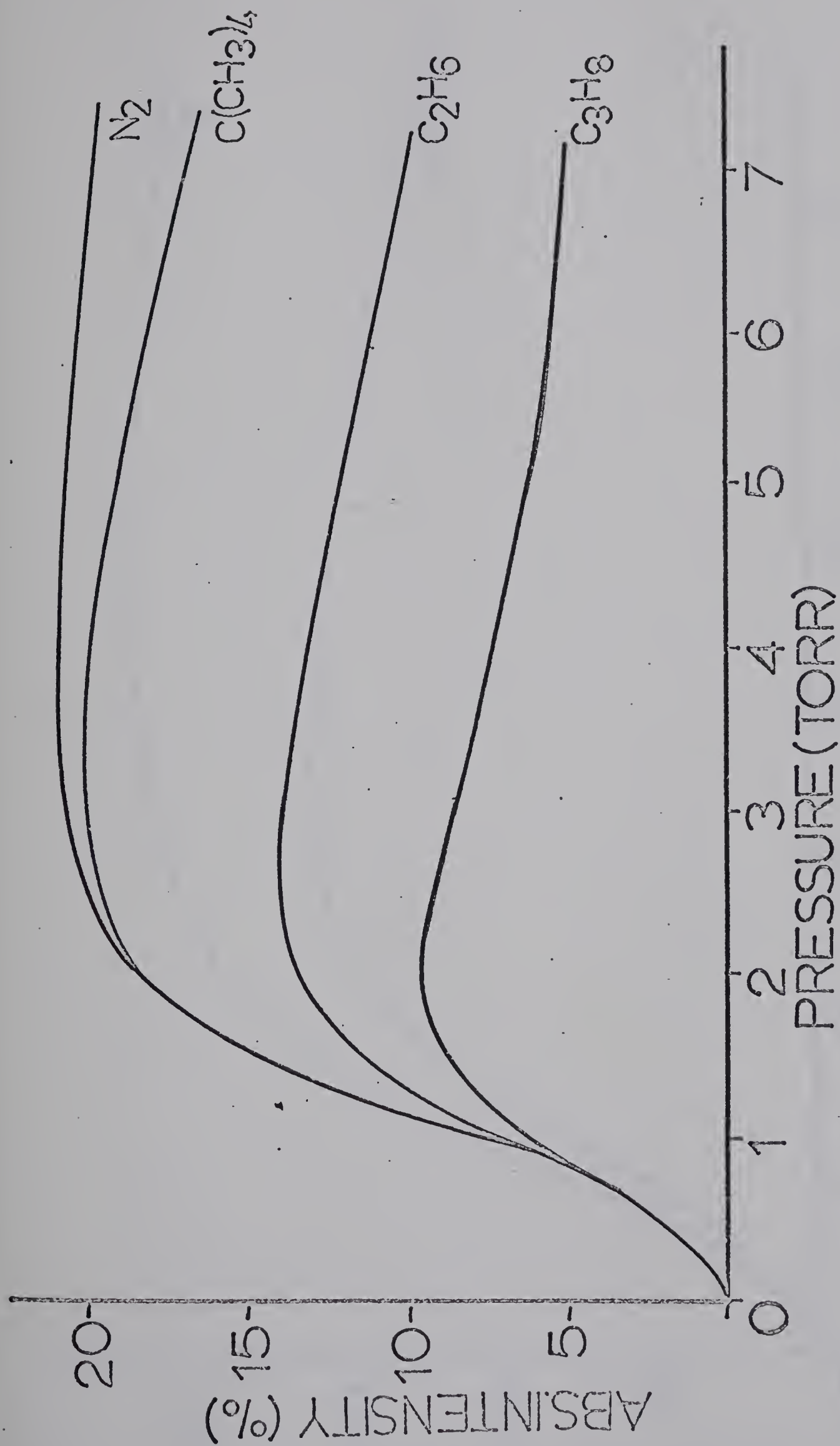


Figure 43. 4047A absorption in 0.1% RH- N_2 mixtures.

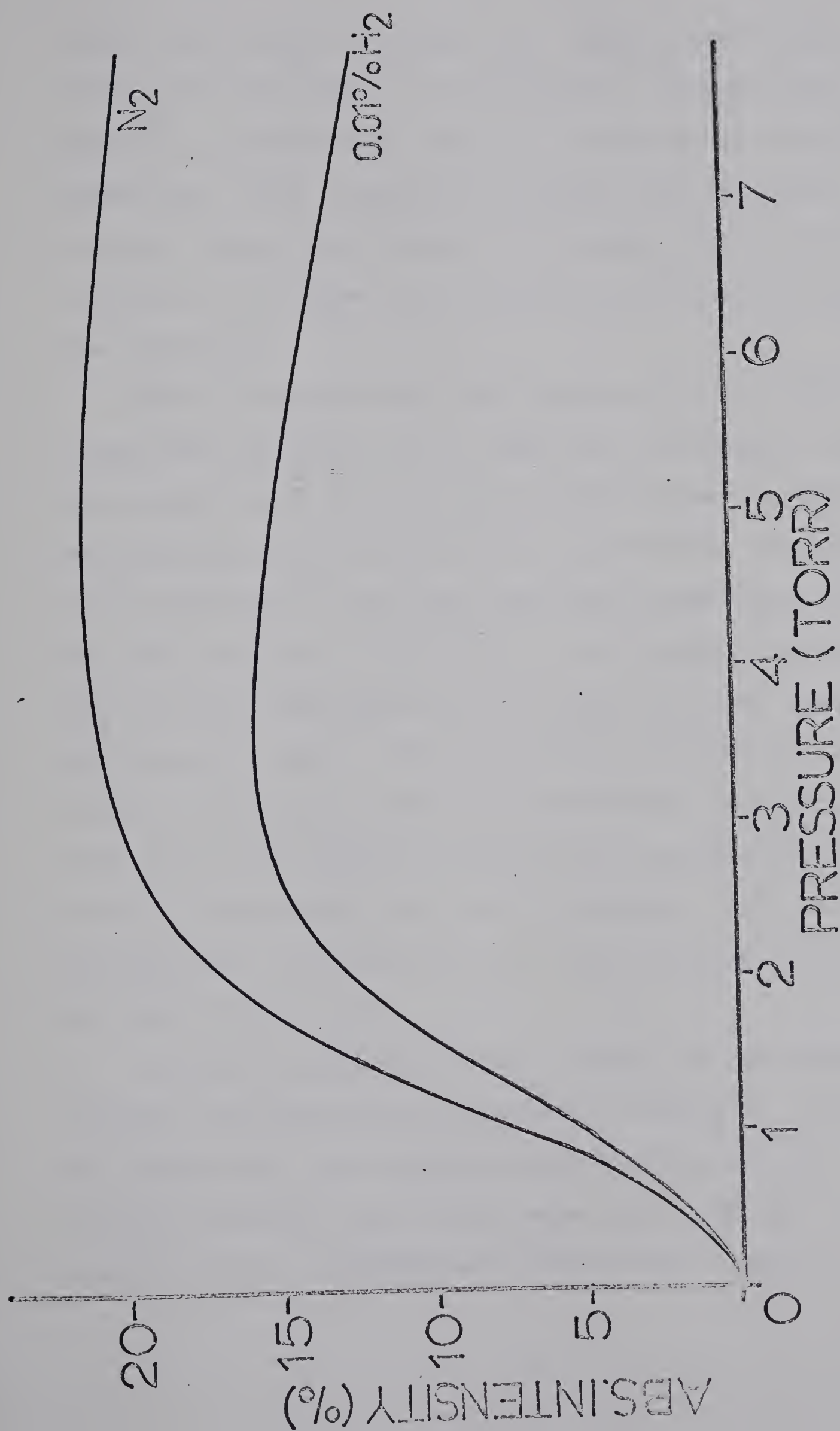


Figure 44. The quenching of Hg^0 atoms in nitrogen diluted with 0.1% hydrogen.

differ by a factor of about ten. Neopentane is the least efficient remover of metastable atoms and the presence of metastable atoms were observed with this substrate. This observation suggests the existence of some relationship between the steady state concentration of Hg^0 atoms and the rate of Hg^0 quenching by the substrate.

Where the quenching rate constant for the $\text{Hg}^1 +$ neopentane reaction was the same as, for example, propane, the steady state concentration of Hg^0 atoms was decreased by approximately eleven fold in the mixture, therefore their detection in the pure substrate became difficult. The participation of Hg^0 atoms in the quenching mechanism will only be detectable when the rate of their removal is sufficiently small. Where the mercury metastable atoms could be detected by the 4047A absorption technique, they must have been formed in significant concentration but even in those cases where their presence could not be established, the possibility of their intervention cannot be safely discounted.

Schematic potential energy curves for the energy transfer reactions were displayed in Figure 8. If it is assumed that the decomposition products of the acceptor molecule will be the same with both Hg^1 and Hg^0 atoms, the different reactivities of the

TABLE 7
Comparison of propane and neopentane quenching ratios for Hg^1 and Hg^0 atoms*

	$(\sigma_1^2) \text{ P}$	Relative conc.decrease of Hg^0 atoms	$(\sigma_1^2) \text{ P}$	Ratio of conc.decrease	conc.of Hg^0 atoms
C_3H_8	1.7	68	1.13	11.3	absent
$\text{C}(\text{CH}_3)_4$	1.5	6			present

* The measurement for Hg^0 was carried out from 0.1% RH-N_2 mixtures at 5 torr pressure.

The pure nitrogen reading under the same condition was 19.9%.

two excited mercury species can be discussed in terms of different cross-over efficiencies. Both alternatives, for (21) and against (58) the participation of Hg^0 atoms in the intermediate complex formation have been suggested. Polanyi et al's suggestion of complex formation is more convincing since it is based on spectroscopic evidence. Complex formation would imply that the potential energy surface of $\text{Hg}^0 + \text{RH}$ passes through a minimum value. The difference between Hg^1 and Hg^0 reactivity is apparent from the potential energy curves. The metastable mercury atoms can only decompose RH if the initially formed complex crosses over at either B^1 or C. The efficiency at C is very low and can be ignored. The efficiency at B^1 will therefore determine whether or not Hg^0 atoms can lead to the fragmentation of RH. Since the energy of this cross-over point is above the initial energy content of the complex and appears at high molecular compression, it is expected to be of low efficiency. In contrast, the complex involving Hg^1 atoms have a higher initial energy content, consequently this interaction will lead more frequently to the fragmentation of the acceptor.

If the acceptor structure is altered so that the cross-over point energy at A changes, the shift of B^1 will be in the same direction. This effect is illustrated by the example of deuterium substitution. The replacement of hydrogen with deuterium shifts the cross-over point energy toward higher values, a result of the greater bond strength of C-D. Since the shift of B^1 takes place in the same direction, the reactivity of Hg^0 atoms will be lowered by deuterium substitution.

The very low reactivity of the nitrogen with Hg^0 is related to the absence of the cross-over A, a consequence of the high bond energy of nitrogen. Similarly carbon monoxide also has a large bond energy, but in contrast to nitrogen it is very reactive towards Hg^0 . This, different behavior of CO is related to the deeper $Hg^1 + CO$ potential energy well (Figure 45). This suggestion is supported by the observation of IR (21), rather than U.V. emission (See Table 2). The result of the deep potential well will be an additional cross-over point at D. Sheer and Fine (34)

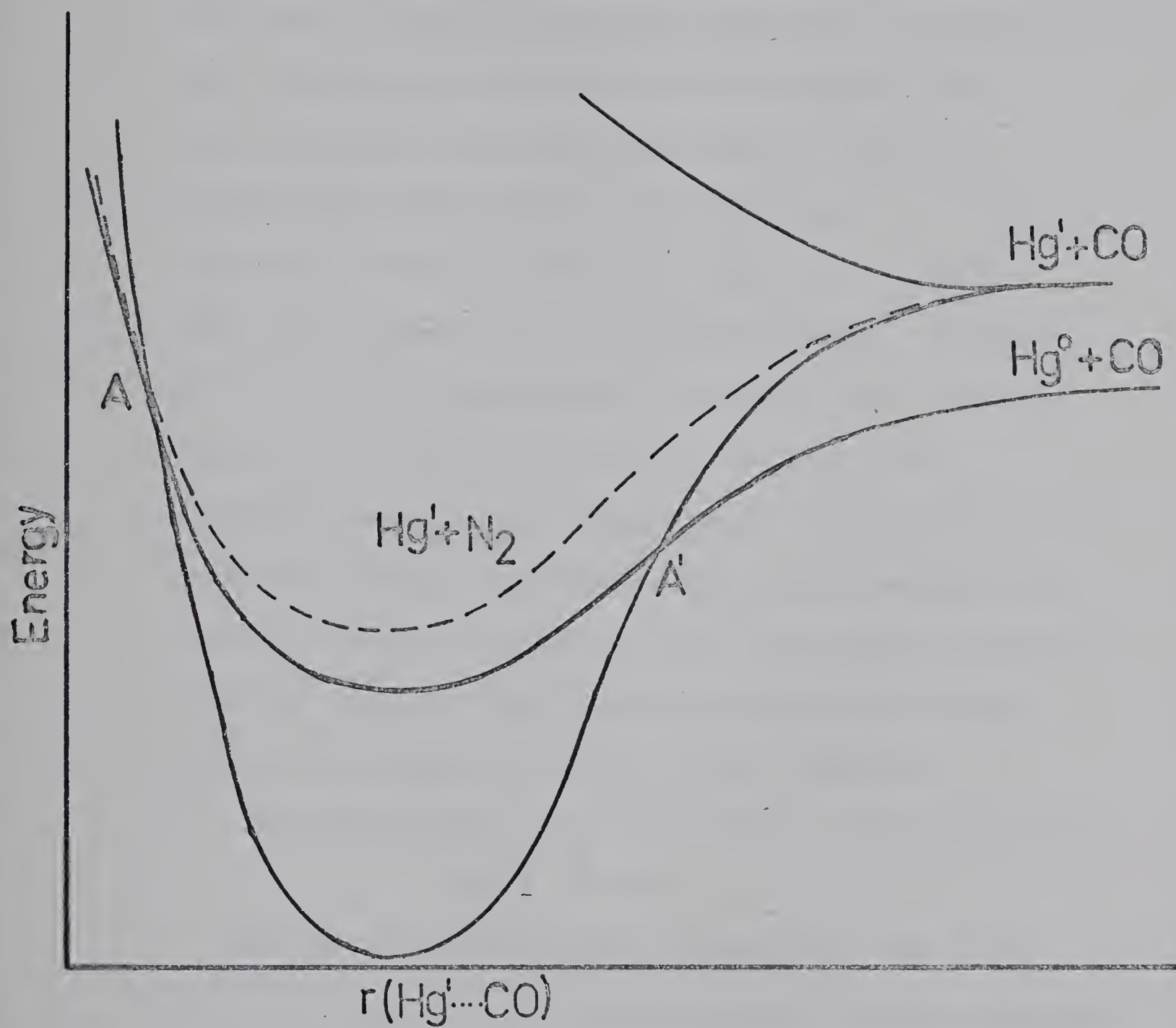


Figure 45. A schematic representation of $\text{Hg}^1 + \text{CO}$ potential energy curves.

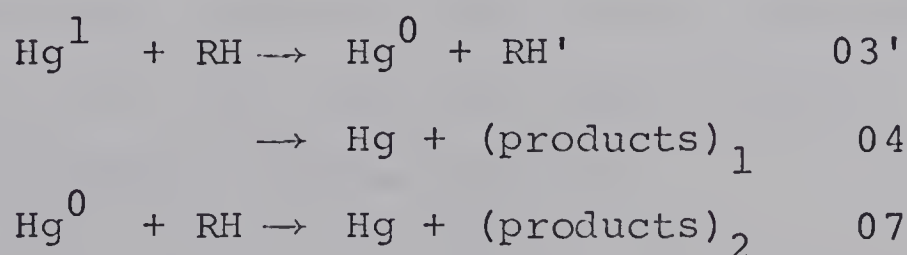
reported that the rate of Hg^0 formation in CO is slightly larger than in N_2 .

If a complex, involving Hg^0 atoms can form, the rate of decay via cross-over at B is probably very small and furthermore it is similar for both nitrogen and carbon monoxide. Since CO reacts more efficiently with Hg^0 atoms, it must then be related to the cross-over at D which does not appear in the nitrogen system. Polanyi et al's. (21) observation supports this theory, that an IR rather than a U.V. emission was detected indicating a deep energy well of $\text{Hg}^1 + \text{CO}$ potential energy surface. Homer and Lossing (58) found no chemical evidence for the complex formation with Hg^0 atoms. Their observation could be the result of a short lifetime of the complex.

ii Calculation of the rate constant for the process.



The previously proposed mechanism, see page has to be modified for hydrocarbon-nitrogen mixtures. The additional steps are:



where:

RH' is a vibrationally excited molecule, products₁ and products₂ are reaction products which may be the same.

Consider hydrocarbons, for which $k'_3, k'_5 \approx 0$, i.e. the metastable atoms are formed by nitrogen only. Using the steady state approximation, and neglecting k'_3 :

$$\begin{aligned} \frac{I_a}{Hg} \approx & \frac{k_{05} k_{02}}{k_{03} (N_2)^2} + \frac{k_{02} k_{06}}{k_{03} (N_2)} + \frac{k_{02} k_{07} (RH)}{k_{03} (N_2)} + \frac{k_{08} k_{02}}{k_{03}} (Hg) \\ & + \frac{k_{04} k_{06} \frac{1}{4} (RH)}{k_{03} (N_2)} + \frac{k_{04} k_{08} (Hg) (RH)}{k_{03}} + \frac{k_{05}}{(N_2)} + k_{06} + k_{07} (RH) \\ & + k_{08} (Hg) (N_2) + \frac{k_{04} k_{05} (RH)}{k_{03} (N_2)^2} + \frac{k_{04} k_{07} (RH)^2}{k_{03} (N_2)} \end{aligned} \quad (III-15)$$

The concentration of RH has to be low in order that its effect upon reaction (08) can be neglected, and where this is so, the last two terms in the steady state expression may be omitted.

Consider an arbitrary set of conditions: $(RH) = 10^{-3}(N_2)$ and a pressure of 5 torr. Substituting all known rate constants and the arbitrary values we obtain from Equation III-15 for the hydrocarbon-nitrogen mixture;

$$\left(\frac{I_a}{Hg^0} \right)_{M; 5mm} = 403 + 9.25 \times 10^{-7} k_4 + 9.28 \times 10^{-3} k_7 \quad \text{III-20}$$

and from Equation III-12 for the nitrogen alone,

$$\left(\frac{I_a}{Hg^0} \right)_{N_2; 5mm} = 403 \times 10^2 \quad \text{III-21}$$

Since the experimentally observed values for Hg^0 atom concentration are relative, the correction factor can be eliminated by dividing Equation III-16 by III-17:

$$\frac{(Hg^0)_{N_2}}{(Hg^0)_M} = \frac{403 + 9.25 \times 10^{-7} k_4 + 9.28 \times 10^{-3} k_7}{403} \quad \text{III-22}$$

where:

k_4 is the quenching rate constant for Hg^1 , Hg^0 values can be obtained from the 4047A absorption; hence the unknown k_7 can be calculated.

The validity of Eq. III-22 is illustrated by the examples of ethane and propane in Appendix I/iii.

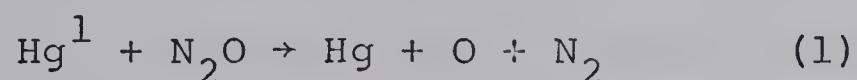
(For example; ethane $k_{O7} = 1.04 \times 10^4 \text{ mm}^{-1} \text{ sec}^{-1}$, propane $k_{O7} = 0.12 \times 10^6 \text{ mm}^{-1} \text{ sec}^{-1}$).

It should be emphasized that this mathematical treatment is applicable only to those systems where the only source of Hg^0 atoms is reaction (03). Agreement with the published values is remarkably good considering that an entirely different experimental technique was used.

8. The comparison of Hg^1 quenching cross sections measured by the physical and by the chemical method.

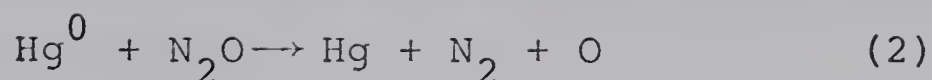
The physical method monitors the decrease of the resonance phosphorescence in the presence of a quencher. It is concerned with the depopulation of the emitting electronic level, regardless of the route by which the decay takes place. The quenching cross section value obtained by this method accounts for the sum of all the decay routes of the emitting species.

The chemical method is based on the competitive quenching of nitrous oxide with a substrate. It assumes that the only source of nitrogen is from the reaction



This assumption is of doubtful validity since the above reaction may also proceed with metastable

atoms,



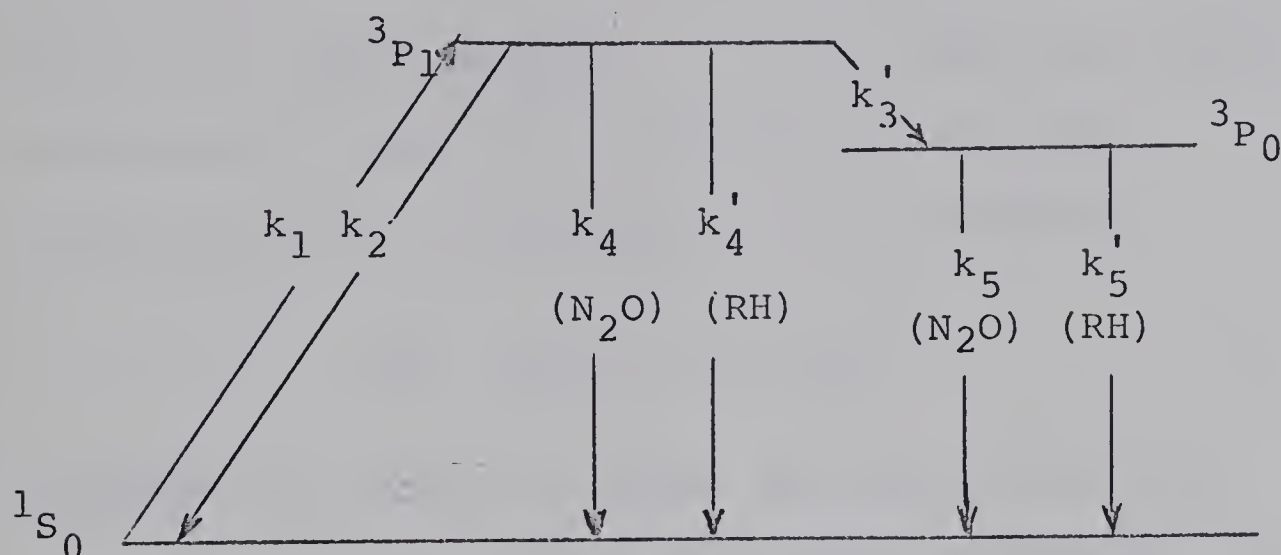
It has been suggested that the metastable atoms in photosensitization have a minor role (19). While this is probably true in many cases, its relative importance in quenching cross section measurements may not be entirely negligible. If metastable atoms are present, and their major mode of decay is via reaction 1, the nitrogen formed by this process will decrease the quenching cross section value. When, for example, the quenching cross sections of compounds A and B are compared and A does not form Hg^0 atoms at the same rate as B, the participation of reaction (2) will have varying importance for each compound. It is important to recognize that the relative scale of quenching cross section values obtained by the chemical method will depend on whether or not the reaction



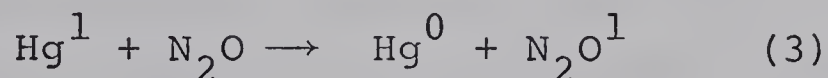
occurs. The physical quenching cross section includes that of reaction 3 but the chemical cross sections usually do not include that of process (3).

The following example will further illustrate the above argument. Consider that the quenching cross

section of compound A is to be determined by both methods. The quenching reactions can be represented by the following scheme:



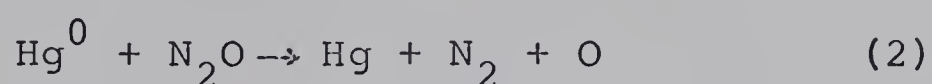
The rate constant for the reaction



was previously reported to be zero (30), and it was confirmed in this laboratory.

When both rate constants, k_3 and k_3' are zero, then both chemical and physical methods measure the direct quenching to the ground state. In the chemical method k_4' is compared to k_4 , while the physical method compares k_4' to k_2 . Therefore the results will be identical provided that k_4 and k_2 are on the same comparative basis (13). When $k_3' \neq 0$, the physical method measures $k_3' + k_4'$, and since the chemical method only considers k_4' , this results in a smaller

quenching cross section value from the latter method. In addition Callear and Williams (35) reported that N_2O reactivity with Hg^0 atoms is greater than any other known compound. If Hg^0 atoms are formed, they will be removed preferentially by N_2O , therefore the contribution of the reaction



becomes appreciable. Since the quenching cross section is obtained from the slope of the $1/\Phi_{\text{N}_2}$ vs. $\text{RH}/\text{N}_2\text{O}$ plot, the increase in nitrogen yield decreases the slope, and hence the chemical quenching cross section value is smaller where Hg^0 atoms can be detected. This conclusion is in agreement with the observations listed in Table 8, that when Hg^0 atoms were detected, the chemical quenching cross section was the lower of the two values. There are a few examples where the chemical value is smaller despite the apparent failure in detecting the presence of metastable atoms. In these instances the differences between the physical and chemical values are small, and with the exception of light and heavy cyclopropane, are within the range of experimental error.

TABLE 8

Compounds that form metastable atoms and
their quenching cross sections.

Compounds	2 $\delta c.$	2 $\delta p.$	$(\text{Hg}^{\text{O}})_r^*$
$\text{CH}_3\text{CH}_2\text{CH}_3$	1.6	1.7	N.D.**
$\text{CD}_3\text{CH}_2\text{CD}_3$	1.4	1.5	1
$\text{CH}_3\text{CD}_2\text{CH}_3$	0.23	0.59	2
$\text{CD}_3\text{CD}_2\text{CD}_3$	0.12	0.49	3
neo- C_5H_{12}	0.92	1.5	5
neo- C_5D_{12}	0.40	--	7
CH_3OH	2.0	8.0	4
$\text{C}_2\text{H}_5\text{OH}$	4.9	18.	2
cyclo C_6H_{12}	11.	13.	N.D.
cyclo C_6D_{12}	0.8	4.7	4
cyclo C_3H_6	0.34	1.1	N.D.
cyclo C_3D_6	0.40	1.0	N.D.
n-butane	4.9 (adopted)	4.9	N.D.
for comparison N_2			19.0

* This column represents the relative value for $\text{Hg}6^3\text{P}_0$ concentration as measured by 4047A transmittance, taking the value for nitrogen as 19%.

** Not detected.

CHAPTER IV SUMMARY AND CONCLUSIONS.

The behaviour of mercury atoms in mercury photosensitized reactions were examined.

The transfer of the absorbed light energy to the acceptor molecule has been the subject of much discussion. It was proven experimentally, in a number of cases, that the energy transfer takes place via the formation of an excited intermediate. The initial interaction results in reversible complex formation and the net forward rate is promoted either by internal relaxation or by an increase in third body concentration. The effect of a third body was shown to be that of increasing the excited complex concentration with pressure. Internal relaxation is an important process, since it explains the exceptional ability of certain C-H bonds to quench. The energy distribution involves some form of coupling between the site of interaction and adjacent bonds; thus quenching cannot be regarded as a process independent of other parts of the molecule. If the interaction involves a centrally located bond it will have a greater probability of coupling than with terminal C-H bonds. This preference, of quenching at the secondary or tertiary, rather than at the primary hydrogens, was seen in the kinetic isotope effect. For example, the unexpectedly large

quenching cross section of neopentane, compared to that of ethane, is the result of a greater rate of internal relaxation.

The quenching cross section expresses the decrease of resonance phosphorescence intensity of Hg^1 atoms, therefore it is a measure of the rate of intermediate complex formation. Equation III-6 was obtained by a steady state approximation assuming a reversible intermediate complex formation. It differs from the well-known Stern-Volmer formula in that it contains the rate of formation and the lifetime of the intermediate as additional factors.

A schematic representation of $\text{Hg}^1 + \text{RH}$ potential energy surfaces is displayed in Figure 8. This qualitative model can explain a number of observations;

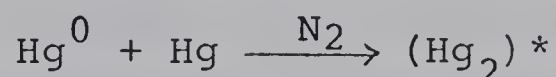
- (a) the quenching of Hg^1 atoms proceeds through the formation of an excited intermediate, which may decay by;
 - i. the fragmentation of the acceptor to yield ground state mercury atoms,
 - ii. the formation of Hg^0 atoms and an excited RH molecule,
 - iii. emission.
- (b) in the adopted experimental method, the emission was used to detect the presence of the intermediate. If a(i) i and (a)ii

are efficient processes, the emission intensity might have been lower than the experimental detection limit, i.e. intermediate formation may have taken place even in those cases where emission was not detected.

- (c) if the cross-over point B^1 is above the initial energy of the intermediate, emission and the formation of Hg^0 atoms will be the chief quenching processes. The nature of the acceptor will determine their relative importance. For example; in CF_4 , emission; and in N_2 , Hg^0 formation dominate, while in $C_3D_2H_6$ both processes occur.
- (d) secondary hydrogen bonds, which are effective in quenching Hg^1 atoms to produce the complex, are also efficient in forming Hg^0 atoms and in increasing the emission intensity.
- (e) when a substitution decreases the cross-over efficiency to the potential surface leading to product formation (because of an increase in bond energy), a larger fraction of the initially formed complex will decompose via Hg^0 atom formation and emission (e.g. propane compared to propane d_2).

- (f) where the cross-over to the potential surface leading to product formation is lower than the donor energy i.e. $< 112\text{kcal}$, the initially formed complex must relax if products are formed in appreciable yield. However, the intermediate involving Hg^0 atoms has a lower energy than that required for the cross-over to the same potential surface. Furthermore it occurs at greater molecular compressions, so that the reactivity of Hg^0 atoms is always less than that of Hg^1 atoms. If products do not form as e.g. in nitrogen, the Hg^0 reactivity with the substrate will be very small.
- (g) when the acceptor molecule has n or π orbitals, the equipartition of the initial complex energy can take place if the complex readily stabilizes, a large quenching cross section value will be observed (e.g. sulphur compounds, aromatics etc.,).

Although nitrogen does not react with Hg^0 atoms, with increasing N_2 pressure the concentration of metastable atoms shows a decrease (see Figure). This is assumed to be due to the reaction



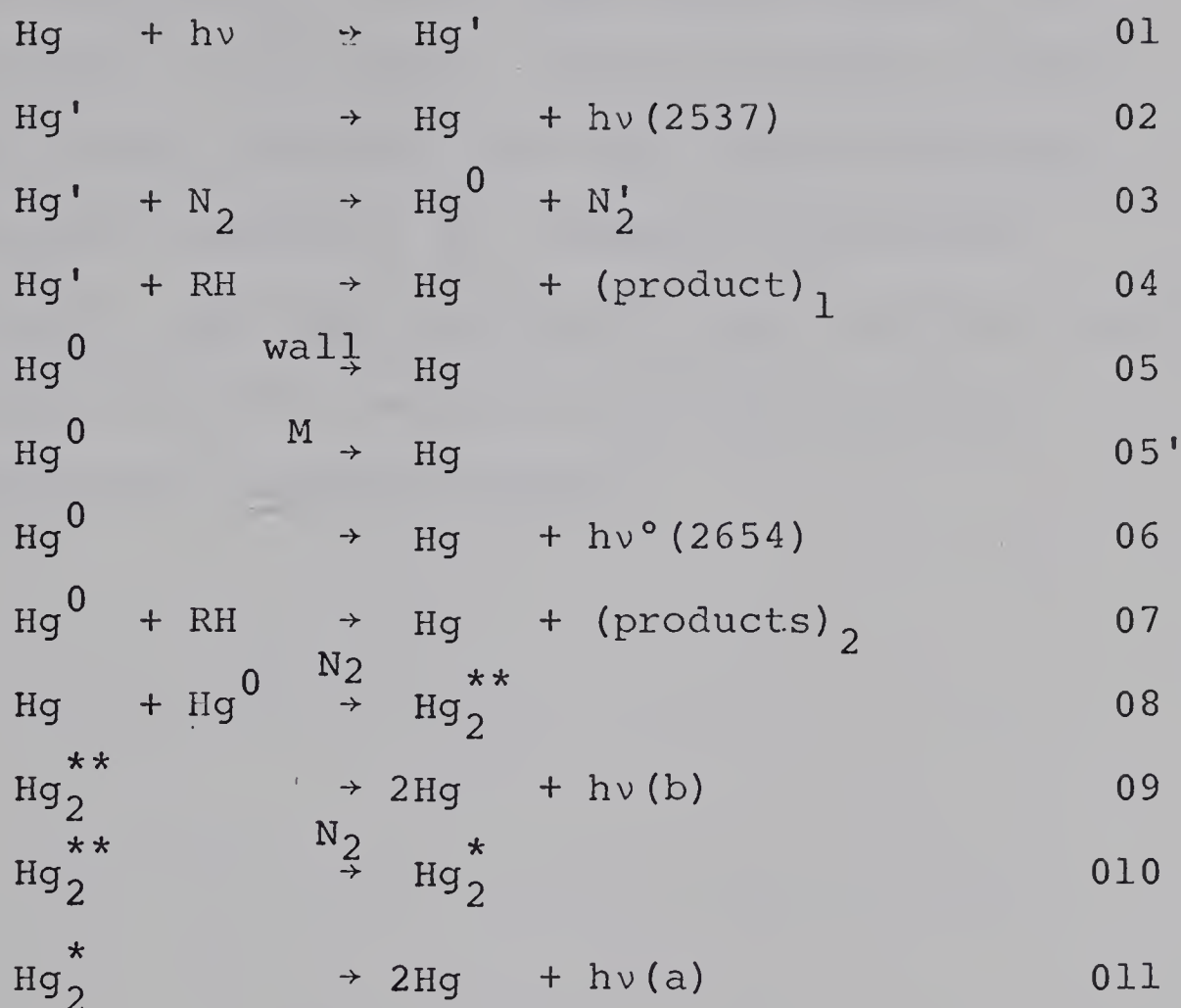
The mercury molecule decays via two emissions - an "a" band (maximum $\sim 4850\text{\AA}$), and a "b" band (maximum $\sim 3350\text{\AA}$). The study of the emissions led to the

conclusion that two distinct spectroscopic levels are present, supporting Mzorowski's view.

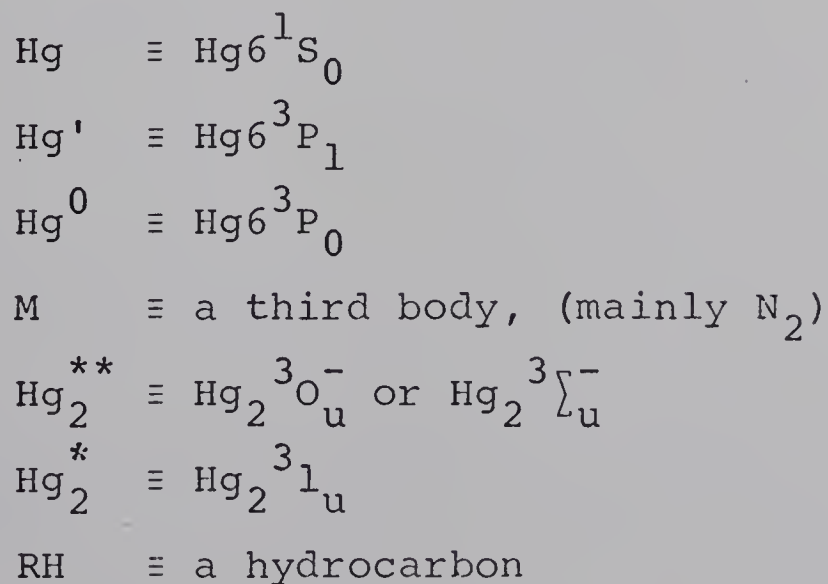
A complete reaction mechanism was proposed incorporating the formation of a mercury diatomic excimer and Hg^0 atom formation. The steady state treatment yielded Eq.III-9 , Eq.III-10 , and Eq.III-11 and their computation gave the predicted linear relationship with pressure. The third order rate constant calculated by two different methods agreed to within the order of magnitude. It had a value of 3.06×10^{-30} cc molec.⁻²sec⁻¹, which is in good agreement with McCoubrey's value and was of the expected magnitude for a third order rate constant.

The addition of a quenching gas decreased the Hg^0 concentration, consequently the molecular emission also decreased. In the ammonia system, where Hg^0 atoms were believed to be formed, the 4047A absorption could not be detected because of the interference from $\text{Hg}^1 + \text{NH}_3$ intermediate emission. However, detection of the "a" band served as experimental evidence of the presence of Hg^0 atoms in the system.

The effect of added ethane and propane on the $(\text{Hg}_2)^*$ emission intensities and on Hg^0 atom concentration was studied. The numerical values for the quenching rate of Hg^0 atoms for both gases were in agreement with those of Callear and Williams.

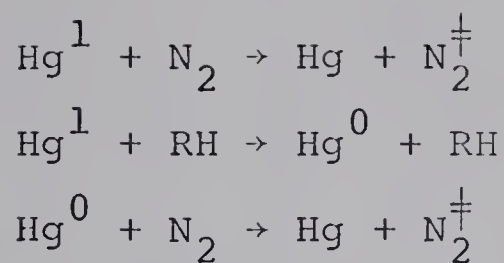
Appendix1. Calculation of rate constants

where the notations are



Assumed from experimental observations, the following reaction rates are near or equal to zero

It was shown that the discrepancy between the physical and chemical methods of quenching cross section measurement is, in some cases, related to the presence of Hg^0 atoms. Since N_2O reacts faster with Hg^0 atoms than with any other known compounds, the reaction leading to N_2 formation may become significant. Nitrogen produced by this reaction results in a lower value of the quenching cross section measured by the chemical method.



k'_{05} to be small compared to the competing rates,
the rate of 05 is $\frac{k_{05}}{(N_2)}$; where (N_2) represents the pressure
of N_2

Using the steady state treatment

$$I_a = k_{02}[\text{Hg}'] + k_{03}[\text{N}_2][\text{Hg}'] + k_{04}[\text{Hg}'][\text{RH}]$$

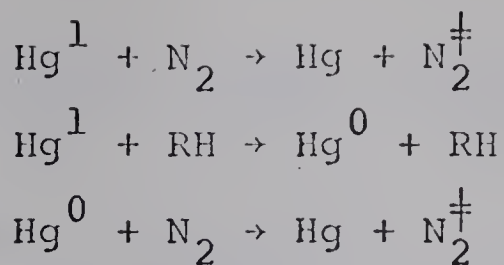
$$[\text{Hg}'] = \frac{I_a}{k_{02} + k_{03}(\text{N}_2) + k_{04}(\text{RH})}$$

$$\begin{aligned}k_{03}[\text{Hg}'][\text{N}_2] &= \frac{k_{05}}{(\text{N}_2)}[\text{Hg}^0] + k_{06}[\text{Hg}^0] + k_{07}[\text{Hg}^0][\text{RH}] \\ &+ k_{08}[\text{Hg}][\text{Hg}^0][\text{N}_2]\end{aligned}$$

$$[\text{Hg}^0] = \frac{k_{03}[\text{N}_2]}{\frac{k_{05}}{(\text{N}_2)} + k_{06} + k_{07}(\text{RH}) + k_{08}[\text{Hg}][\text{N}_2]} \times \text{Hg}'$$

Substitute and take the reciprocals

$$\begin{aligned}\frac{1}{\text{Hg}^0} &= \frac{1}{I_a k_{03}(\text{N}_2)} \left\{ \left[\frac{k_{05}}{(\text{N}_2)} + k_{06} + k_{07}(\text{RH}) + k_{08}(\text{Hg})(\text{N}_2) \right] \right. \\ &\quad \left. \times [(k_{02} + k_{03}(\text{N}_2) + k_{04}(\text{RH}))] \right\}\end{aligned}$$



k'_{05} to be small compared to the competing rates,
 the rate of 05 is $\frac{k_{05}}{(N_2)}$; where (N_2) represents the pressure
 of N_2

Using the steady state treatment

$$I_a = k_{02}[\text{Hg}'] + k_{03}[\text{N}_2][\text{Hg}'] + k_{04}[\text{Hg}'][\text{RH}]$$

$$[\text{Hg}'] = \frac{I_a}{k_{02} + k_{03}(N_2) + k_{04}(\text{RH})}$$

$$\begin{aligned}
 k_{03}[\text{Hg}'][\text{N}_2] &= \frac{k_{05}}{(N_2)}[\text{Hg}^0] + k_{06}[\text{Hg}^0] + k_{07}[\text{Hg}^0][\text{RH}] \\
 &\quad + k_{08}[\text{Hg}][\text{Hg}^0][\text{N}_2]
 \end{aligned}$$

$$[\text{Hg}^0] = \frac{k_{03}[\text{N}_2]}{\frac{k_{05}}{(N_2)} + k_{06} + k_{07}(\text{RH}) + k_{08}[\text{Hg}][\text{N}_2]} \times \text{Hg}'$$

Substitute and take the reciprocals

$$\begin{aligned}
 \frac{1}{\text{Hg}^0} &= \frac{1}{I_a k_{03}(N_2)} \left\{ \left[\frac{k_{05}}{(N_2)} + k_{06} + k_{07}(\text{RH}) + k_{08}(\text{Hg})(N_2) \right] \right. \\
 &\quad \left. \times [(k_{02} + k_{03}(N_2) + k_{04}(\text{RH}))] \right\}
 \end{aligned}$$

$$\begin{aligned}
\frac{I_a}{\text{Hg}^0} = & \frac{1}{k_{03}(\text{N}_2)} \left(\frac{k_{05}k_{02}}{(\text{N}_2)} + k_{06}k_{02} + k_{02}k_{07}(\text{RH}) + k_{08}k_{02}(\text{Hg})(\text{N}_2) \right. \\
& + \frac{k_{05}k_{04}(\text{RH})}{(\text{N}_2)} + \frac{k_{04}k_{06}(\text{RH})}{(\text{N}_2)} + k_{01}k_{04}(\text{RH})^2 \\
& + k_{08}(\text{Hg})(\text{N}_2)k_{04}(\text{RH}) + \frac{k_5}{(\text{N}_2)} + k_{06} + k_{07}(\text{RH}) \\
& \left. + k_{08}(\text{Hg})(\text{N}_2) \right)
\end{aligned}$$

rearranging

$$\begin{aligned}
\frac{I_a}{\text{Hg}^0} = & \frac{k_{05}k_{02}}{k_{03}(\text{N}_2)^2} + \frac{k_{02}k_{06}}{k_{03}(\text{N}_2)} + \frac{k_{02}k_{07}(\text{RH})}{k_{03}(\text{N}_2)} + \frac{k_{08}k_{02}}{k_{03}}(\text{Hg}) \\
& + \frac{k_{04}k_{05}(\text{RH})}{k_{03}(\text{N}_2)^2} + \frac{k_{04}k_{06}(\text{RH})}{k_{03}(\text{N}_2)} + \frac{k_{04}k_{07}(\text{RH})^2}{k_{03}(\text{N}_2)} \\
& + \frac{k_{04}k_{08}(\text{Hg})(\text{RH})}{k_{03}} + \frac{k_{05}}{(\text{N}_2)} + k_{06} + k_{07}(\text{RH}) + k_{08}(\text{Hg})(\text{N}_2)
\end{aligned}$$

i) consider case, when $(\text{RH}) = 0$

Therefore

$$\begin{aligned}
\frac{I_a}{(\text{Hg}^0)} = & \frac{k_{05}k_{02}}{k_{03}(\text{N}_2)^2} + \frac{k_{02}k_{06}}{k_{03}(\text{N}_2)} + \frac{k_{08}k_{02}}{k_{03}}(\text{Hg}) + \frac{k_{05}}{(\text{N}_2)} + k_{06} \\
& + k_{08}(\text{Hg})(\text{N}_2)
\end{aligned}$$

at minimum

$$\frac{d(I_a/\text{Hg}^0)}{d(\text{N}_2)} = 0$$

$$-\frac{2k_{05}k_{02}}{k_{03}(N_2)^3} - \frac{k_{02}k_{06}}{k_{03}(N_2)^2} - \frac{k_{05}}{(N_2)^2} + k_{08}(\text{Hg}) = 0$$

or

$$k_{08}(\text{Hg})(N_2) = \left(\frac{k_{02}k_{06}}{k_{03}} + k_{05} \right) (N_2)^2 - \frac{2k_{05}k_{02}}{k_{03}} = 0$$

Since:

$$\begin{aligned} k_{06} &= 133 \text{ sec}^{-1} \quad () \\ k_{02} &= 0.9 \times 10^6 \text{ sec}^{-1} \text{ (corrected for imprisonment)} \\ k_{03} &= 2.1 \times 10^5 \text{ mm sec}^{-1} \quad () \\ k_{05} &= 206 \text{ mm sec}^{-1} \quad () \\ [\text{Hg}] &= 1.2 \times 10^{-3} \text{ mm} \end{aligned}$$

after computing

$$\begin{aligned} \frac{k_{02}k_{06}}{k_{03}} + k_{05} &= 7.86 \times 10^2; \quad 2\frac{k_{05}k_{02}}{k_{03}} = 1.77 \times 10^3 \\ k_{08} &= \frac{7.86 \times 10^2 (N_2)^2 + 1.77 \times 10^3}{(N_2)^3 [\text{Hg}]} \end{aligned}$$

Taking $(N_2)_m = 7$ from Figure ; substitute and compute for

k_{08}

$$\begin{aligned} k_{08} &= 1.84 \times 10^4 \text{ mm}^{-2} \text{ sec}^{-1} \text{ or} \\ &1.71 \times 10^{-29} \text{ cc}^2 \text{ mole}^{-2} \text{ sec}^{-1} \end{aligned}$$

ii) The alternate calculation for the rate (8) considers the steady state approximation for Hg^0 atoms only.

At pressures α and β

$$(I_a^0)_\alpha = \frac{k_{05}}{(\alpha)} (\text{Hg}^0)_\alpha + k_{06} (\text{Hg}^0)_\alpha + k_{08} (\text{Hg}) (\text{Hg}^0)_\alpha (\alpha)$$

$$(I_a^0)_\beta = \frac{k_{05}}{(\beta)} (Hg^0)_\beta + k_{06} (Hg^0)_\beta + k_{08} (Hg) (Hg^0)_\beta (\beta)$$

Since the Hg^0 concentration is related to the 4047 absorption, its original concentration is determined by the competition of reaction (2) and (3), therefore

$$f = \frac{k_{03} [Hg^1] [N_2]}{k_{02} [Hg^1] + k_{03} [Hg^1] [N_2]}$$

or

$$f = \frac{(N_2)}{N_2 + \frac{k_{02}}{k_{03}}}$$

The value for $\underline{f}$ can be computed for α and β , furthermore

$$(I_a^0)_\beta = \frac{f(\beta)}{f(\alpha)} (I_a^0)_\alpha$$

thus the ratio

$$R = \frac{k_{06} + k_{05}/(\alpha) + k_{08} (Hg) (\alpha)}{k_{06} + k_{05}/(\beta) + k_{08} (Hg) (\beta)} \times \frac{(Hg^0)_\alpha}{(Hg^0)_\beta}$$

where $R = f(\alpha)/f(\beta)$

$(Hg^0)_\alpha = f(\alpha) (Hg_r^0)$ where Hg_r^0 = the relative conc. of Hg^0 atoms determined by the 4047 abs.

Taking a set of values for α and β

(3,27); (3,24); (3,21); (3,18); (3,15); (3,12);

(6,21); (6,27).

after computation the obtained set of values given in the

same order

$$(3.12, 3.11, 3.30, 3.22, 3.88, 3.89, 3.07, 2.91) \times 10^3$$

or the average value for k_{08}

$$3.31 \times 10^3 \text{ mm}^{-2} \text{ sec}^{-1} \text{ or } 3.06 \times 10^{-30} \text{ lc}^2 \text{ molec}^{-2} \text{ sec}^{-1}$$

Consider the case, when RH is present in the nitrogen and note

$$(\text{RH}) / (\text{N}_2) = j$$

$I_{\text{N}_2}^r, I_M^r$ the relative rates of Hg^0 formation

in pure nitrogen and in the mixture respectively.

The expression for pure nitrogen is

$$I_{\text{N}_2}^r = \frac{k_{05}k_{02}}{k_{03}(\text{N}_2)^2} + \frac{k_{02}k_{06}}{k_{03}(\text{N}_2)} + \frac{k_{08}k_{02}}{k_{03}}(\text{Hg}) + \frac{k_{05}}{(\text{N}_2)} + k_{06} + k_{08}(\text{Hg})(\text{N}_2)$$

or substitute numerical values

$$I_{\text{N}_2}^r = \frac{0.88 \times 10^3}{(\text{N}_2)^2} + \frac{7.86 \times 10^2}{(\text{N}_2)} + 17 + 201.2 + 3.98(\text{N}_2)$$

Considering an arbitrary value for $\text{N}_2 = 5 \text{ mm}$; k_{08} adopted from calculation of steady state treatment,

$$I_{\text{N}_2}^r = 4.03 \times 10^2$$

For I_M^r compute the above equation using $j = 10^{-3}$

$$I_M^r = 403.3 + 9.25 \times 10^{-7} k_{04} + 9.28 \times 10^{-3} k_{07}$$

Combine the equations

$$\frac{I_M^r}{I_{N_2}^r} = \frac{403.3 + 9.25 \times 10^{-7} k_{04} + 9.28 \times 10^{-3} k_{07}}{403.3}$$

(iii) Calculate k_{07} for

<u>Ethane</u> ,	k_{04}	$= 0.83 \times 10^5 \text{ mm}^{-1} \text{ sec}^{-1}$
Readings:	I_M^r	$= 18.52$
	$I_{N_2}^r$	$= 14.71$

substitute these values and ignore the term involving k_{04}

$$k_{07} = 1.04 \times 10^4 \text{ mm}^{-1} \text{ sec}^{-1}$$

Callear and Williams obtained $\frac{k_{04}}{k_{07}} = 10$

The above calculation gives

$$\frac{0.83}{0.10} = 8.3$$

<u>Propane</u> ,	k_{04}	$= 0.985 \times 10^6 \text{ mm}^{-1} \text{ sec}^{-1}$
Readings:	I_M^r	$= 45.45$
	$I_{N_2}^r$	$= 10.42$

substitute, but consider the term involving k_{04}

$$k_{07} = 0.12 \times 10^6 \text{ mm}^{-1} \text{ sec}^{-1}$$

Callear and Williams obtained $k_{04}/k_{07} = 10$

The above calculation

$$\frac{0.98}{0.12} = 8.2$$

2. The steady state treatment for the excimer emission bands.

Since the rate of formation must be equal to the rate of disappearance

$$k_{08} [\text{Hg}] [\text{Hg}^0] [\text{N}_2] = k_{09} [\text{Hg}_2^{**}] + k_{10} [\text{Hg}_2^{**}] [\text{N}_2]$$

or

$$[\text{Hg}_2^{**}] = \frac{k_{08} [\text{Hg}] [\text{Hg}^0] [\text{N}_2]}{k_{09} + k_{10} (\text{N}_2)}$$

However the intensity of band "b"

$$\begin{aligned} I(b) &= k_{09} [\text{Hg}_2^{**}] \\ &= \frac{k_{09} k_{08} [\text{Hg}] [\text{Hg}^0] [\text{N}_2]}{k_{09} + k_{10} (\text{N}_2)} \end{aligned}$$

$$\frac{1}{I(b)} = \frac{1}{k_{08} [\text{Hg}] [\text{Hg}^0] [\text{N}_2]} + \frac{k_{10}}{k_{08} k_{09} [\text{Hg}] [\text{Hg}^0]} ;$$

or rearranging

$$\frac{[\text{N}_2] [\text{Hg}^0]}{I(b)} = \frac{1}{k_{08} [\text{Hg}]} + \frac{k_{10}}{k_{08} k_{09} [\text{Hg}]} (\text{N}_2)$$

Considering the relationship

$$\frac{I(a)}{I(b)} = \frac{k_{10} [Hg_2^{**}] [N_2]}{k_{09} [Hg_2^{**}]}$$

Expressing $I(b)$

then rearranging

$$\frac{[N_2]^2 [Hg^0]}{I(a)} = \frac{k_{09}}{k_{10} k_{08} [Hg]} + \frac{1}{k_{08} [Hg]} [N_2]$$

Role of $\text{Hg}(^3P_0)$ Atoms in Mercury Photosensitization*

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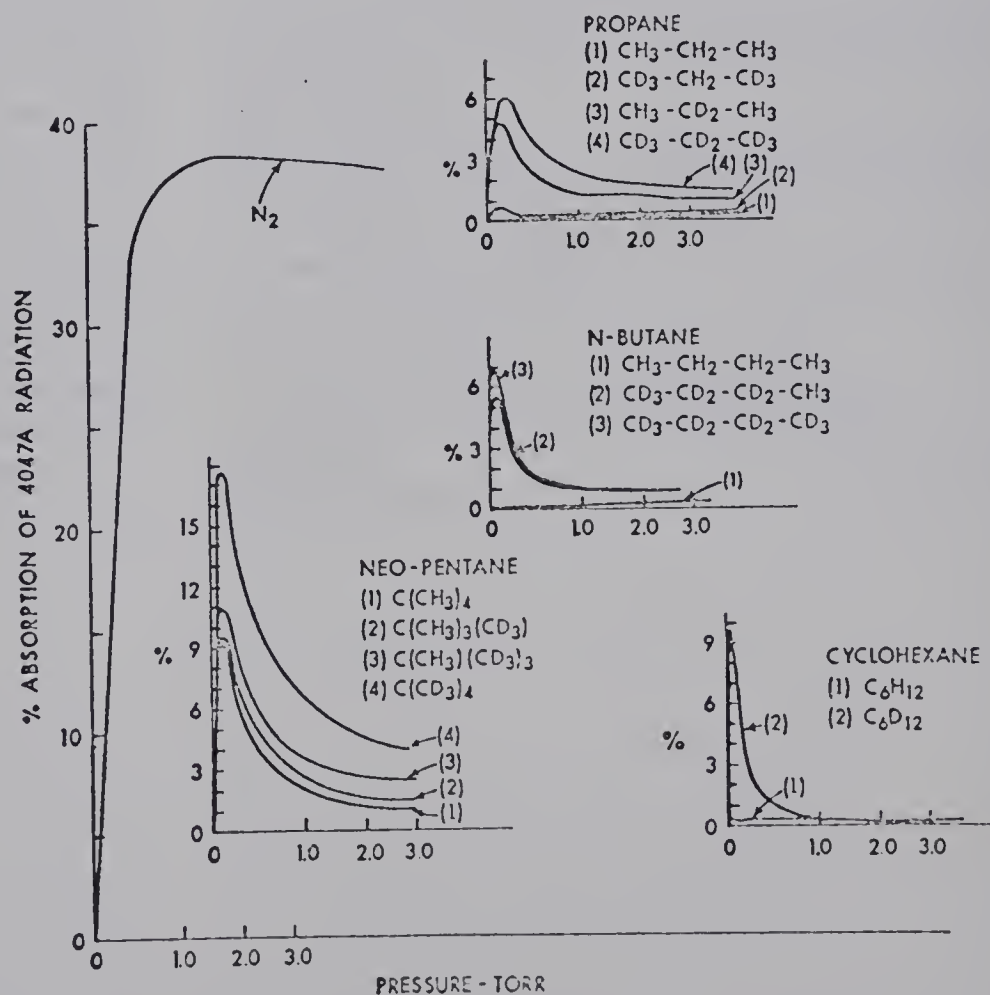
THE role of metastable 3P_0 atoms in mercury photosensitization has been the subject of much discussion.¹ Metastable atoms have thus far been detected only in systems (N_2 , CO , D_2O , and H_2O)² which are characterized by their chemical inertness. Thus the question as to whether 3P_0 atoms play a more general role in mercury sensitization has long awaited experimental study. We have recently succeeded in detecting 3P_0 atoms in a number of important systems, a preliminary description of which is given here.

Our interest in 3P_0 atoms arose from the observations^{3,4} that a serious discrepancy exists between the physical⁵ and chemical⁶ quenching cross section values for the 2537-Å mercury radiation in certain systems.

These discrepancies have been explained as being due to the participation of metastable mercury atoms in the reaction. In this connection we have measured the quenching cross section of a number of deuterated paraffins by the physical method and found consistently higher values than are obtained by the chemical method. Consequently, we have attempted the direct detection of $\text{Hg}(^3P_0)$ atoms in these systems and have found that, in most cases where the chemical cross section is less than the physical one, $\text{Hg}(^3P_0)$ atoms were present in relatively high concentration.

Two methods of detecting 3P_0 atoms were used: (a) the absorption of 4047-Å light using apparatus similar to that of Kimbell and LeRoy^{2a} and (b) the

FIG. 1. 4047-Å absorption intensities vs substrate pressure for nitrogen, propane, *n*-butane, *neo* pentane, cyclohexane, and their deuterated derivatives. The relative concentrations of $\text{Hg}(^3P_0)$ atoms are related to the absorption intensities by Beers law up to ~20% absorption.



absorption of 2967-Å light in flash experiments after Callear.⁷

The 4047-Å absorption apparatus was tested by flowing N₂ through the cell; absorption intensities of 20% or higher could be obtained. Next the absorption intensities were determined with eight deuterated paraffins. In each case the presence of ³P₀ atoms could be detected. With light paraffins, in general, no significant absorption appeared, the exception being neopentane, which induced strong absorption of the 4047-Å radiation.

In the flash photolysis experiments a 50-cm cell and a 41 and 3μF capacitors (at 10 kV) were used. The spectrum was recorded on a photographic plate in a medium quartz spectrograph. The absorption line of the mercury was pressure broadened by 970-Torr krypton. No absorption at 2967 Å was observed. However, a weak absorption at 2967 Å was detected when 8.7-Torr neo-C₅H₁₂ was added to the krypton, confirming the presence of ³P₀ atoms in the system. Experiments were also done with 515-Torr krypton and 1.7-Torr cyclo-C₆D₁₂ and again a weak absorption at 2967 Å was detected.

4047-Å absorption intensities versus pressure are plotted for a number of substrates in Fig. 1 and the pertinent data are summarized in Table I. It is seen that Hg ³P₁ atoms are quenched to the ³P₀ state more efficiently by deuterated than by light paraffins. Neo-C₅H₁₂ is of particular interest since at low pressures (<300 μ) it produced a 4047-Å absorption intensity considerably larger than that obtained from N₂ at an equal pressure. At higher pressures (>300 μ), however the absorption sharply declined indicating an efficient removal of metastable atoms through quenching by neopentane. This was confirmed by the observation that the steady-state concentration of ³P₀ atoms from 2.4 Torr of N₂ (22% absorption) was reduced to less than half (10%) upon addition of 48 μ of neopentane. Thus it appears that in the photosensitization of this molecule, decomposition is mainly initiated by Hg (³P₀) atoms (φ primary ≥ 0.87).⁸ With light propane, cyclohexane, *iso*- and *n*-butane, on the other hand, ³P₀ atoms appear to play at the most a minor role in the process. Thus no general correlation is yet apparent to predict the significance of ³P₀ atoms in a given system.

Discrepancies between the physical and chemical

TABLE I. Cross section values and the concentration of Hg³P₀ atoms.

	Absorption			
	4047 Å	2967 Å	Σ ² phys Å ²	Σ ² chem Å ²
CH ₃ CH ₂ CH ₃	Absent		1.5 ^a	1.5 ^c
CH ₃ CD ₂ CH ₃	Medium		0.54	0.23 ^c
CD ₃ CH ₂ CD ₃	Very weak		1.3	1.4 ^c
CD ₃ CD ₂ CD ₃	Medium		0.43	0.12 ^c
<i>n</i> -C ₄ H ₁₀	Absent		4.9 ^a	...
CD ₃ CD ₂ CD ₂ CH ₃	Medium		1.7	0.45 ^d
<i>iso</i> -C ₄ H ₁₀	Absent		4.9 ^b	6.5 ^b
neo-C ₅ H ₁₂	Strong	Present	1.5 ^b	0.91 ^d
neo-C ₅ D ₁₂	Very strong		...	0.07 ^d
cyclo-C ₃ H ₆	Very weak		1.1	0.34 ^d
cyclo-C ₃ D ₆	Very weak		1.0	0.39 ^c
cyclo-C ₆ H ₁₂	Very weak		12	11 ^d
cyclo-C ₆ D ₁₂	Strong	Present	4.3	0.78 ^d

^a See Ref. 4.

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^d See Ref. 3.

cross-section values may indicate the presence of ³P₀ atoms. In the nitrous oxide-substrate system, the ³P₀ atoms produced by the substrate will be quenched in subsequent competing reactions with the substrate or nitrous oxide, leading to an apparent cross-section value characteristic for the over-all process. The physical method on the other hand provides a value which is a measure of the combined efficiency of deactivation of the ³P₁ state to the metastable and ground states.

* The financial support of the National Research Council of Canada is gratefully acknowledged.

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Fluorescence of Excited Complex Molecules in Mercury Photosensitization

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THE process of energy transfer from excited mercury atom¹ according to the nature of the energy-acceptor molecule can be classified broadly into two groups: (a) electronic excitation transfer, with molecules having low-lying triplet states; these usually contain π , or nonbonding orbitals ($C=C$, $C=O$, etc.), and (b) conversion of electronic energy of the excited Hg atom directly into chemical form, which is exemplified by the paraffins. With regard to the latter, two views have developed, one of which envisaged the process as being an abstraction-type reaction, $RH + Hg^* \rightarrow R + HHg \rightarrow R + H + Hg$, while the other considered the possibility of the formation of an excited complex precursor $(RH \cdot Hg)^*$. The principal difference between the two mechanisms is that the former requires the transfer of the total excitation energy of Hg $6(^3P_1)$ atoms to the acceptor while the latter would allow partial energy transfer, as well as provide a mechanism for energy dissipation from the system via fluorescence: $(RH \cdot Hg)^* \rightarrow RH^+ + Hg + h\nu$, to account for lower than unit quantum efficiencies. Observance of fluorescence could therefore have a decisive role in distinguishing between these alternatives.

In the early literature on mercury photosensitization a number of scattered reports² have appeared describing fluorescence attributed to $Hg(^3P_1) + M \rightarrow (Hg \cdot M)^* \rightarrow Hg + M + h\nu$.

For these reasons we have made a careful search for emission from $Hg(^3P_1)$ atoms with a representative series of compounds.

A cylindrical Spectrosil resonance cell, 12 by 140 mm, with plain parallel LiF windows at the ends, was attached to a vacuum system. Hg vapor, pure or mixed with the substrate, was flowed through the cell at variable pressures. The latter was monitored by an Atlas MMCT vacuum gauge and recorded on the x axis of a Hewlett-Packard X-Y recorder. The y axis registered the output of a 1P28 RCA photomultiplier placed in front of the end window of the cell to measure the intensity of the fluorescence. The exciting source was

a pair of water-cooled resonance lamps, from which the radiation was perpendicular to the cell axis. The equipment was constructed to minimize scattered light reaching the photomultiplier by use of collimators, condensor lenses, and shielding. The photomultiplier was used in conjunction with either a 2800- or 3100-Å (± 100 half-width) interference filter or a Bausch & Lomb 500-mm grating monochromator, with a slitwidth of 3 nm, which allowed only a very crude spectral analysis.

A feeble but well-reproducible emission was observed with a number of paraffins (cf. Fig. 1), in the spectral region of ~ 2400 – 2800 Å. The true spectrum must be much narrower, probably in the range of 2537 to ~ 2600 Å, but better resolution could not be achieved with the present equipment without serious sacrifices in the signal-to-noise ratio. Plots of relative fluorescence intensities (with the 2800-Å filter) versus substrate pressure are displayed in Fig. 1. Since the shape of emission contour does not vary significantly with substrate, the relative emissivities in the figure are probably directly comparable. Deuteration affects the emission yields in an irregular manner. Methane and neopentane show no isotope effect, while with ethane the

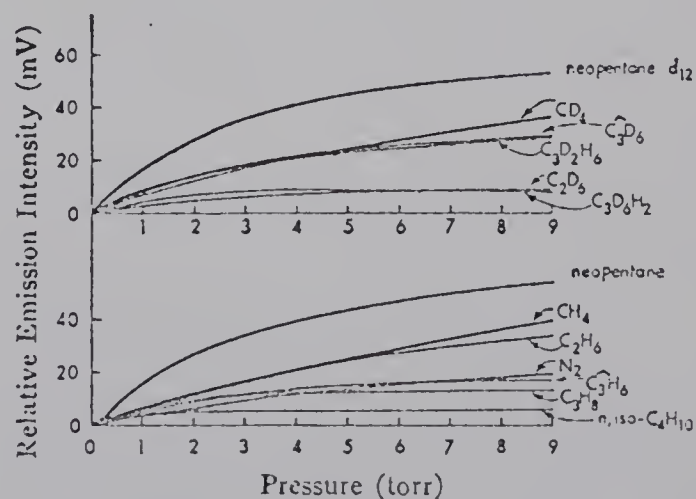


FIG. 1. Relative emission intensities as a function of energy-acceptor pressure.

TABLE I. Summary of results.

Substrate	Emission	
	Region (Å)	Rel. intensity
H ₂ , D ₂		nil
NO, CO		nil
C ₂ H ₄ , C ₂ F ₄		nil
C ₂ HF ₃ , C ₂ H ₂ F ₂		nil
C ₂ H ₃ F, CH ₃ CHO		nil
CF ₄	2540-2600	~½ of CH ₄
H ₂ O, D ₂ O	2537-3200	100× of the paraffin emission
NH ₃ , ND ₃	2900-4000	100× of the paraffin emission
Ar, Kr, Xe	2540 to about 3100	100× of the paraffin emission

emission decreases and with cyclopropane increases on deuteration.

A number of other compounds were also investigated and the results are summarized in Table I. With substrates producing Hg (³P₀) atoms³ (H₂O, NH₃, N₂, neopentane, etc.), the excimer emission bands (due to Hg₂^{*}) at 3340 and 4850 Å have also appeared strongly.

Small amounts of NO had no effect on the emission from paraffins or NH₃; consequently the emission cannot be ascribed to free radicals. Also, the emission intensities were linearly dependent on the exciting light intensities. For these reasons we are forced to conclude that these emissions originate from the excited complex molecules formed between a substrate molecule (atom) and an excited Hg(³P₁) atom. There is no apparent correlation between the ability of the substrate to produce Hg(³P₀) atoms and the molecular emission intensities, and furthermore the emission spectra in most cases extend below the emission line of the meta-stable atoms (2650 Å).

The lifetime of the excited molecular complex at least in the case of propane has to be short (<10⁻⁹ sec) since no deactivating effect was apparent up to 500 torr pressure.

The significance of these observations in mercury photosensitization reactions will have to be assessed from further studies.

We wish to thank the National Research Council of Canada for financial support.

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Kinetics of the "a" and "b" Band Emissions of Mercury Excimers

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The two long-wavelength end emission continua, the "a" band ($\lambda_{\max} \sim 4850 \text{ \AA}$) and the "b" band ($\lambda_{\max} \sim 3350 \text{ \AA}$), appearing in optically excited mercury vapor have been assigned by Mrozowski² to the $^1\Sigma_g^+ \leftarrow ^1^3O_u^-$ and $X^1\Sigma_g^+ \leftarrow ^1^3^1_u$ transitions, respectively, of the diatomic-mercury excimer molecules. More recently, McCoubrey³ has questioned these assignments and postulated both bands to arise from the $A^3O_u^-$ state, the former by a pressure-induced transition and the latter by a spontaneous transition to the ground state. These postulates were based on studies of pure mercury vapor at elevated temperatures and relatively high pressures.

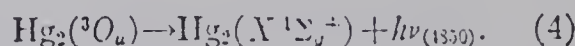
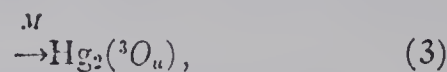
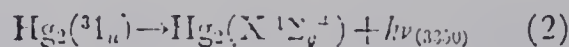
We report here the kinetic behavior of the two emission continua in relation to the steady-state concentration of $\text{Hg}(^3P_0)$ atoms at room temperature and low mercury concentrations in the presence of added N_2 , H_2O , D_2O , neopentane, etc.

The apparatus and experimental technique were described in a previous Communication.⁴ The "a" band was isolated by a Corning CR 3385 cutoff filter and the "b" band by a Kodak 18A and a 0.5-mm Plexiglass combination.

Our first observation was that the bands appeared when and only when the 4047- $\text{\AA}$ line absorption indicated the presence of $\text{Hg}(^3P_0)$ atoms. The intensity ratios were pressure dependent and for N_2 and D_2O , I_a/I_b was a linear function of pressure, as seen from Fig. 1.

On the other hand, paraffins had a distinctly different effect; I_a/I_b fell off rapidly with increasing pressure. The fact that N_2 , H_2O , D_2O , Xe, etc., enhance I_a/I_b but paraffins suppress it requires the intervention of two emitting excited states in the mechanism, thereby

favoring Mrozowski's original suggestion²



Steady-state treatment predicts the following relations:

$$[\text{N}_2][\text{Hg}^0]/I_{3350} = (k_2/k_1k_3[\text{Hg}][\text{N}_2] + (k_1[\text{Hg}])^{-1}), \quad (I)$$

$$[\text{N}_2][\text{Hg}^0]/I_{4850} = (k_1[\text{Hg}])^{-1}[\text{N}_2] + (k_2/k_1k_3[\text{Hg}]), \quad (II)$$

and

$$I_{4850}/I_{3350} = (k_3/k_2)[\text{N}_2]. \quad (III)$$

The linearity of the experimental plots (cf. Fig. 1) indicates the success of the mechanism.

Consider formation of $\text{Hg}(^3P_1)$ atoms by absorption of the 2537 $\text{\AA}$ resonance radiation (5), their decay by spontaneous emission (6) and collisional relaxation to the 3P_0 level by nitrogen (7), spontaneous emission (8) and diffusion to the wall (9) of the 3P_0 atoms along with step (1) and taking $k_7^6 = 2.1 \times 10^7 \text{ mm}^{-1} \cdot \text{sec}^{-1}$, $k_8^7 = 1.33 \times 10^2 \text{ mm}^{-1} \cdot \text{sec}^{-1}$, $k_9^7 = 2.06 \times 10^2 \text{ mm} \cdot \text{sec}^{-1}$, and applying Holstein's formula⁵ for the imprisonment effects, the third-order rate constant k_1 is equal to $3.06 \pm 1.2 \times 10^{-30} \text{ cc}^2 \text{ atoms}^{-2} \cdot \text{sec}^{-1}$. This may be compared to the value of 1.0×10^{-30} found by McCoubrey³ for mercury as chaperone, and 1330×10^{-30} by McAlduff and Leroy⁷ for nitrogen.

The value of the ratio k_3/k_2 is 0.14 mm^{-1} . If the lifetime of the $\text{Hg}_2(^3^1_u)$ molecule is $\sim 1 \times 10^{-7} \text{ sec}$, k_3 becomes $\sim 6.6 \times 10^{-14} \text{ liters molecules}^{-1} \cdot \text{sec}^{-1}$, corresponding to about one effective collision out of four.

The present mechanism, though well accommodating the experimental observations, is oversimplified; indications are that nitrogen also quenches both emission bands.

We would like to thank the National Research Council of Canada for their financial support.

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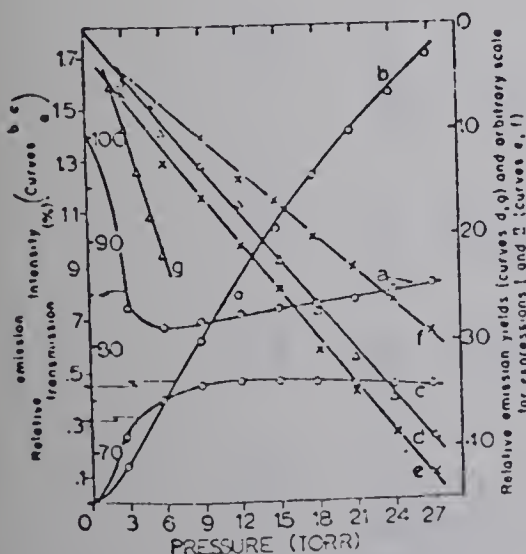


FIG. 1. (a) Relative intensities of 4047- $\text{\AA}$ transmission; (b) relative intensities of 4850- $\text{\AA}$ band emission; (c) relative intensities of 3350- $\text{\AA}$ band emission; (d) $I(4850)/I(3350)$; (e) Expression I; (f) Expression II [(a)-(f) in the presence of nitrogen]; (g) $I(4850)/I(3350)$ in the presence of D_2O . (Similar results were obtained with H_2O , NH_3 , and neopentane.)

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